2022

CARBON CAPTURE PROGRAM R&D
COMPENDIUM
of
CARBON CAPTURE TECHNOLOGY

U.S. DEPARTMENT OF
ENERGY

NATIONAL
ENERGY
TECHNOLOGY
LABORATORY

DISCLAIMER

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OVERVIEW

The U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) administers a comprehensive, multi-pronged approach for carbon management by developing both point source capture (PSC) and carbon dioxide removal (CDR) technologies. When coupled with secure geologic carbon storage or carbon dioxide (CO_2) conversion into long-lasting products, these technologies will support the United States in achieving ambitious goals for a greenhouse gas (GHG)-neutral economy by 2050, a carbon-pollution-free power sector by 2035, and a 50% reduction from 2005 levels in economy-wide net GHG pollution by 2030.

DOE's National Energy Technology Laboratory (NETL) manages both the PSC and CDR Programs. NETL is progressing research and development (R&D) of advanced CO_2 capture technologies for PSC (for fossil fuel-based power generation and industrial sources) and CDR (co-located with low-carbon energy sources).

The PSC Program is developing the next generation of advanced CO_2 capture concepts and accelerating commercially deployable solutions that can be applied to a wide spectrum of CO_2 emissions sources. The deployment of PSC technologies will decarbonize existing infrastructure in the power and industrial sectors, including hydrogen, ethanol, cement, and steel production facilities.

The CDR Program is fostering R&D focused on direct air capture (DAC), biomass carbon removal and storage, and enhanced mineralization, with emerging research in ocean-based CDR. CDR technologies remove CO_2 that has accumulated in the atmosphere and oceans and durably stores it in geologic, bio-based, and ocean reservoirs, or in value-added products, to create negative emissions. This wide array of approaches will help achieve gigaton-scale CO_2 removal by 2050 and support DOE's Carbon Negative Shot goal to remove CO_2 from the atmosphere and geologically store it for less than \$100/net tonne CO_2-equivalent (CO_2e) for at least 100 years.

The Carbon Capture Technology Compendium is compiled biannually to provide a technical summary of CO_2 capture technology R&D sponsored by DOE/NETL's PSC and CDR Programs. The current Compendium presents 124 projects in a single document, all of which were active at some point between October 1, 2019, and October 1, 2021.

The Compendium is organized into three main sections. The first section covers research in the areas of transformational materials development and systems analysis performed by NETL's Research and Innovation Center (RIC). The second section includes projects managed under the PSC Program, organized in subsections based on the application of the technologies (i.e., post-combustion capture and pre-combustion capture from both power generation and industrial sources). The third and final section includes projects managed under the CDR Program, organized in subsections based on the application of the technologies (i.e., DAC, biomass carbon removal and storage, and enhanced mineralization).

Each subsection is arranged by the ending scale of the current R&D effort, from front-end engineering design (FEED) and pre-FEED, to large- and small-scale pilot testing (Technology Readiness Level [TRL] 6–7), to conceptual engineering and materials design at bench and laboratory scale (TRL 2–5). Finally, within the set of projects for each ending scale, the projects are organized by key technology—solvents, sorbents, membranes, hybrid, novel concepts, or enabling technologies.

CARBON CAPTURE TECHNOLOGY SHEETS

RESEARCH AND INNOVATION CENTER TECHNOLOGIES

Ion Gel Membrane for Post-Combustion CO_2 Separation

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new, ultra-high-performance facilitated transport polymer membranes with carbon dioxide (CO_2)/nitrogen (N_2) gas separation performance that lie above the Robeson Upper Bound for post-combustion CO_2 separation. NETL is building a small-scale membrane module using the most promising membrane material and testing it in a real flue gas environment. NETL is also working with industry partners to identify and address potential scale-up issues with the material. Development efforts are consistent with overall goals of reducing the energy penalty and cost of CO_2 separation relative to conventional technologies through economic analysis.

technical goals

- Synthesize, fabricate, and test novel high-performance polymer materials using simulated flue gas.
- Identify an industrial partner for applying to the U.S. Department of Energy (DOE) technology commercialization fund for one high-performance polymer membrane.
- Demonstrate at least one high-performance polymer with a CO_2 permeability of more than 2,000 Barrer and a CO_2/N_2 selectivity of more than 100.
- Complete an economic analysis showing potential to meet transformational carbon capture goal.
- Downselect to a single, most promising membrane material, and complete the fabrication of a module in conjunction with an industry partner.
- Test and complete a membrane module in an actual gas environment in conjunction with an industry partner.

technical content

Membrane technology poses an exciting option for large-scale gas separations due to the small footprint, simplicity of the device and process, ease of operation, modularity and bolt-on installation, and typical low parasitic energy requirements. However, NETL analyses have shown that extremely high permeability membrane materials are needed to make this technology an economically viable option. While there are multiple experimental polymer materials reported in the literature that appear to meet the performance requirements, most have practical drawbacks, such as poor mechanical strength, poor thin-film forming ability, reduced performance with aging, or complex and expensive synthesis procedures. Therefore, there is a need to develop new polymers that have high performance, but that also meet the practical requirements of industrial gas separations.

Most polymer membranes have consistent CO_2 permeance at different CO_2 concentrations (partial pressures) in the to-be-treated gas stream, unless being plasticized at very high pressures. Facilitated transport membranes, however, perform best under water-saturated conditions and are particularly suitable for flue gas carbon capture, where water vapor is often present. An amine-functionalized ion gel membrane, which takes advantage of reversible reactions between CO_2

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Amine-Functionalized Ion Gel Membrane

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402 (Task 9)

predecessor project:

2020 Carbon Capture FWP

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partners:

Idaho National Lab (INJ); University Coalition Texas A&M; Compact Membrane Systems (CMS); National Carbon Capture center (NCCC) and amine, has demonstrated exceptional permeability and selectivity. Furthermore, its excellent water retention capability helps it maintain performance over a wide range of humidity, including survival from intermittent flue gas shutdown, which is difficult for other facilitated transport membranes. However, the permeance reported for this type of membrane is usually low, despite its high permeability. In the proposed work, NETL is transforming high permeability into high permeance through thin-film composite (TFC) development for ion gel membranes.

The development of amine-functionalized ion gel membranes has included the synthesis and optimization of a polymer network, selection and synthesis of amine-functionalized ionic liquids, and membrane fabrication and characterization. While commercial amine polymers are available in the market, these were found to have insufficiently high molecular weight (MW) and degree of hydrolysis (i.e., amine content) to make truly high-performance membranes. Work was performed to refine the synthesis procedure for high yield, scalable high MW precursor polymer through inverse emulsion polymerization. The effect of degree of hydrolysis on the gas transport performance was evaluated. By optimizing the degree of hydrolyzation, NETL can achieve maximum performance that is above the Robeson Upper Bound. NETL amine polymer demonstrated a CO_2 permeability of 616 Barrer and CO_2/N_2 selectivity of 170 while the commercial equivalent only had a CO_2 permeability of 216 Barrer and CO_2/N_2 selectivity of 89. Two ionic liquids were synthesized as mobile carriers. Ion gel bulk films were tested for gas permeance using a humidified mixture of CO_2/N_2 containing 14% CO_2. Ion gel membrane #1 containing commercial polymer and an NETL ionic liquid demonstrated a CO_2 permeability of 903 Barrer and CO_2/N_2 selectivity of 320. Ion gel membrane #2 containing NETL polymer and the same ionic liquid demonstrated CO_2 permeability of 2,010 Barrer and CO_2/N_2 selectivity of 216. Ion gel membrane #3 containing commercial polymer and a second ionic liquid demonstrated CO_2 permeability of 3,315 Barrer and CO_2/N_2 selectivity of 94. The last membrane was tested using CO_2/N_2 mixed gas containing 4% CO_2 to simulate the NGFG conditions and obtained CO_2 permeability of 11,054 Barrer and CO_2/N_2 selectivity of 138, which has far exceeded the project milestone, as well as other state-of-the-art facilitated transport membranes reported in the literature. Future work consists of TFC fabrication and testing using simulated and actual flue gases. An amine-functionalized ion gel membrane, which takes advantage of reversible reactions between CO_2 and amine, has demonstrated exceptional permeability and selectivity.

technology advantages

- Excellent water adsorption capability makes ion gel a good fit for a variety of practical industrial carbon capture.
- Ion gel materials developed by NETL have significantly enhanced separation performance than the ion gels that are reported in the literature.
- Membrane material is suitable to be fabricated into various membrane module forms, such as flat sheet, spiral wound, and hollow fiber.

R&D challenges

- Achieving above Robeson Upper Bound performance.
- Identifying ion gel compositions that have durable mechanical properties and high CO_2 loading capacity.
- Establishing a scalable and reliable fabrication protocol for ion gel TFCs.
- Evaluating the membrane technology under variable environments needed to transfer technology to market.

available reports/technical papers

Kusuma V, Budhathoki S, Baker J, Macala M, Hopkinson D, “Structural Designs of Cross-linked Polymer Network and Ionic Liquids for Ion Gel Gas Separation Membranes,” Presented by NETL at 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, August 2019, *https://www.osti.gov/servlets/purl/1778124*.

Kusuma V, Chen, C, Baker J, Macala M, and Hopkinson D, “The Effect of Poly(Ethylene oxide) Cross-linking Structure on the Mechanical Properties and CO_2 Separation Performance of an Ion Gel Membrane,” United States: N. p., 2019. *https://doi.org/10.1016/j.polymer.2019.121666*.

Baker J, “Effect of Amine Content on the CO_2 Separation Performance of Polyvinylamine Membranes for Flue Gas Carbon Capture,” Presented by NETL at 2021 American Chemical Society Meeting, August 2021, *https://www.osti.gov/servlets/purl/1844405*.

Hollow Fiber Post-Combustion Membrane Modules

primary project goal

The National Energy Technology Laboratory's (NETL) Research and Innovation Center (RIC) is developing new, ultra-high-performance membranes and membrane modules for post-combustion carbon dioxide (CO_2) capture. The objective of this effort is to deliver an optimized hollow fiber membrane module for CO_2 separation from industrial sources under near-ambient pressure conditions. A combination of computational fluid dynamics (CFD) modeling and experimental testing are being used to optimize hollow fiber module design to optimize gas flow distribution, minimize pressure drop, and maximize separation efficiency. The team is using computational tools to optimize the design of the module casing and 3D printing to produce test modules for model validation toward a better fundamental understanding of module design.

technical goals

- Reduce the pressure drop in hollow fiber membrane modules for ambient pressure, post-combustion CO_2 capture.
- Increase the gas permeance performance for membrane modules.
- Reduce the time and effort required to prototype new membrane module designs using 3D printing.

technical content

Due to the low driving force for CO_2 separation in post-combustion flue gas and in many industrial carbon capture applications, any membrane-based separation system that does not use flue gas compression must have modules with very low pressure drop.

This effort is a collaboration between NETL (hollow fiber fabrication, hollow fiber module fabrication, and gas permeance testing) and the University of Toledo (membrane module design and modeling). The University of Toledo is conducting CFD simulations to optimize the configuration of hollow fiber membrane modules for post-combustion CO_2 capture. Parameters such as module size, hollow fiber size, flow configurations, packing configurations, and sweep can be varied to minimize pressure drop and maximize separation efficiency. Initial work focuses on how packing of hollow fiber membranes near the solid wall of an enclosing case affects fluid flow and performance. The work also is being extended to randomly packed fiber bundles for comparison to allow determination of both the effect of gaps between the bundle and wall and the effect of random fiber packing on module performance. The results will provide a basis for establishing module manufacturing specifications. Later work is aimed at addressing the use and effect of multiple fiber tows to form hollow fiber bundles. Fiber tows are groups of up to 100 fibers that move through the membrane manufacturing process together and then are used to build a module fiber bundle. Use of fiber tows creates non-uniform fiber packing that can be detrimental to performance. Further work is focused on optimizing the module casing design, including parameters such as the location and geometry of fluid distribution manifolds, as well as internal shell baffling.

CFD models were developed and used to solve using square- and triangle-packed fiber bundles. These simplified models were developed in such a way that they

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Hollow Fiber Membrane Modules

participant:

National Energy Technology Laboratory–Research and Innovation Center (RIC)

project number:

FWP-1022402 (Task 11)

predecessor project:

2020 Carbon Capture FWP

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partners:

University of Toledo

give the same performance predictions as a full 3D simulation of filled-in square-packed fiber bundles, but with greatly reduced computational requirements. These models capture the effects of poor fiber packing at the interface with the casing on module performance. The solution domains for these modules and the equivalent planar bundle (EPB) are shown in Figure 1. The blue line in the figure separates the bundles into two domains: (1) the fibers closest to the wall/casing (C2/P2) and (2) the rest of the fibers (C1/P1).

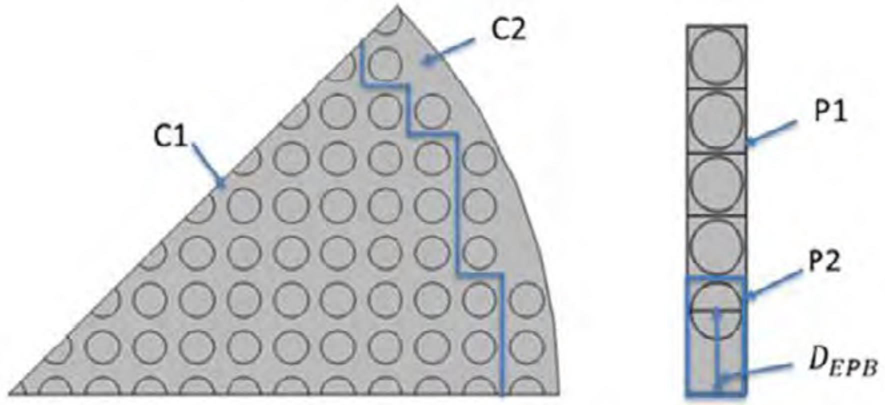

Figure 1: Illustration of circular (left) and planar (right) computational domains.

Simulations were performed over both 3D and EPB domains using a feed gas with 20% CO_2 at a pressure of 2 bar. The performance metrics of these modules, as well as the performance curves of an ideal counter current (ICC) module, are shown in Figure 2. For these metrics, the retentate recovery (R) is indicative of the operational energy costs, while the feed flow rate (F) is indicative of the capital costs of the membrane. R and F are plotted against CO_2 mole fraction in Figure 2. In addition, the performance curve for the 3D square domain is compared to those of the simplified domains in Figures 3 (triangular) and 4 (EPB), respectively.

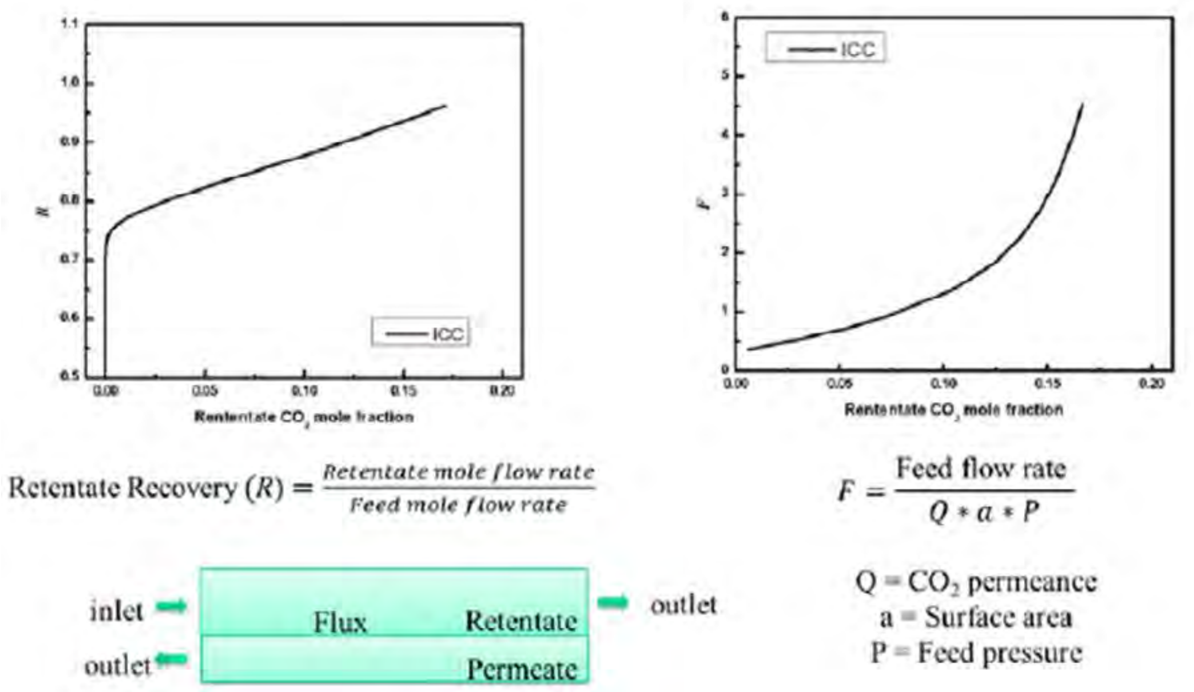

Figure 2: Module performance metrics.

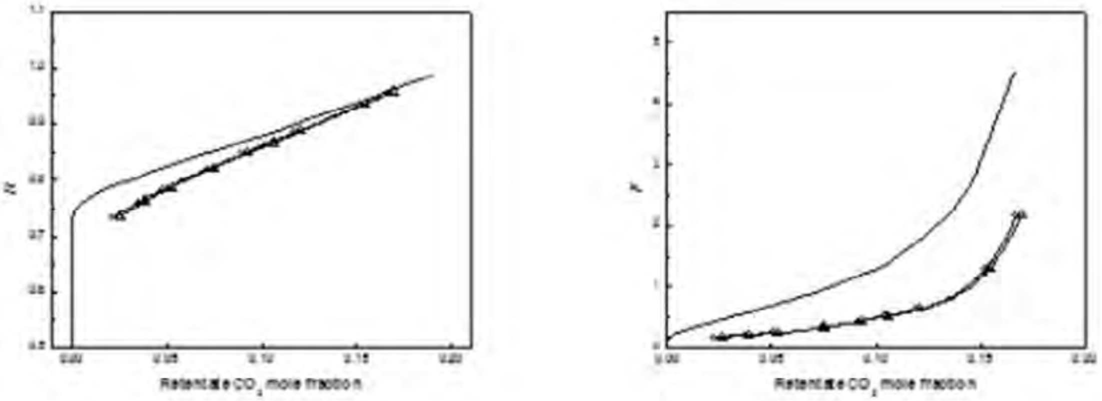

Figure 3: R (left) and F (right) versus CO$_2$ mole fraction for 3D square- and triangular-packed fiber bundles (circles = square packing; triangles = triangle packing) plotted against ICC.

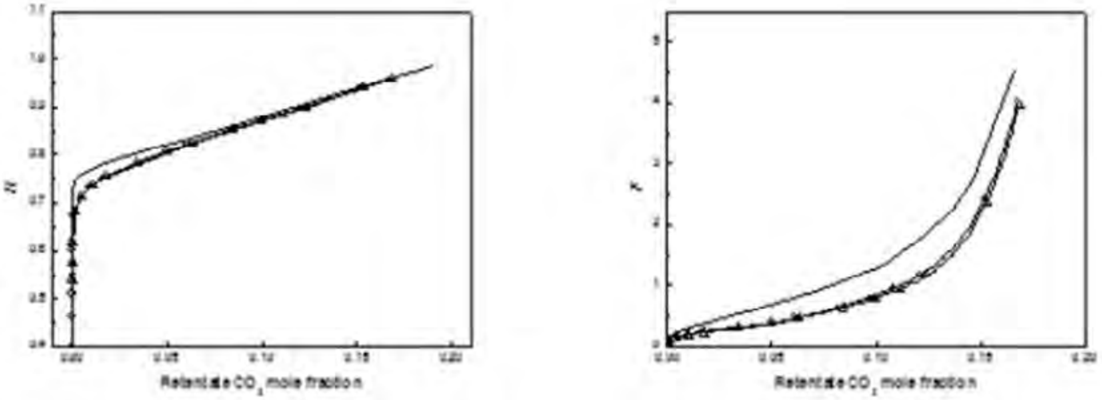

Figure 4: R (left) and F (right) versus CO$_2$ mole fraction for 3D square-packed and EPB domains (circles = square packing; triangles = EPB) plotted against ICC.

Based on these results, NETL plans to continue with modeling these support structures through two additional subtasks: (1) studying axial diffusion effects to better understand when such diffusion is detrimental to membrane performance, and (2) development and testing of 3D-printed modules for experimental performance measurements in order to validate the models developed thus far.

technology advantages

- Improved design of hollow fiber modules for ambient pressure separations.
- Rapid design and fabrication of test modules.

R&D challenges

- Optimizing geometry for minimizing concentration polarization, module length, and dead space while maximizing packing density.
- Achieving representative module performance in a lab-scale configuration.

available reports/technical papers

N/A.

High-Performance Blended Rubbery Membranes

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new, ultra-high-performance membranes and membrane modules for post-combustion carbon dioxide (CO_2) capture. NETL-RIC has performed key research to further develop a rubbery thin-film composite (TFC) membrane with proprietary membrane support.

technical goals

- Develop a scalable TFC membrane for industrial carbon capture that has a CO_2 permeance of at least 3,000 gas permeance units (GPU) and CO_2/nitrogen (N_2) selectivity of at least 25.
- Optimize both the membrane supports and the selective material for scalability, thermal and chemical stability, and anti-aging properties.
- Perform a long-term field test of the developed membranes for at least 500 hours.

technical content

Membrane technology poses an exciting option for large-scale gas separations due to the small footprint, simplicity of the device and process, ease of operation, modularity and bolt-on installation, and typically low parasitic energy requirements. Industrially, polymer-type membranes have a well-established role in gas separation technology, and are commonly used in applications such as separation of hydrogen from gas mixtures, purifying natural gas, etc. However, extremely high-permeance (or high-GPU) membranes are needed to make this technology an economically viable option for post-combustion CO_2 capture. As shown in Figure 1, a recent NETL techno-economic analysis (TEA) shows high-GPU membranes can greatly reduce the costs of CO_2 capture compared to conventional amine sorbents, and the capture cost reduction is extremely sensitive to CO_2 permeance enhancement at the range of 1,000–3,000 GPU when CO_2/N_2 selectivity is maintained above 25. For this project task, NETL-RIC is developing scalable CO_2-selective (CO_2/N_2 selectivity >25) TFC membranes with a CO_2 permeance greater than 3,000 GPU using a novel nanoporous membrane support, a blended rubbery polymer, and optimizing coating methods to integrate these two materials as TFCs.

As shown in Figure 2, NETL has developed a proprietary membrane support (NETL-S6) with high porosity (20%) and small pore sizes (<40 nm). This nanoporous NETL-S6 support provides much greater CO_2 permeance (260,000 GPU), surface porosity, and physicochemical stability than commercial polymer porous supports. NETL-RIC scaled up the NETL-S6 fabrication from 40 cm^2 per sheet in Execution Year (EY) 2020 to 200 cm^2 per sheet in EY 2021.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Rubbery Thin-film Composite Membrane

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402 (Task 21)

predecessor project:

N/A

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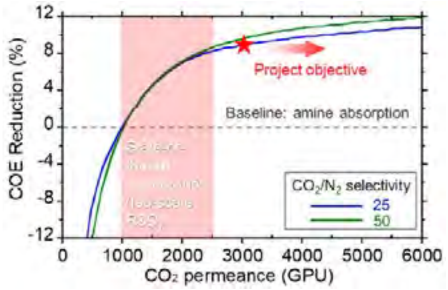

Figure 1: Cost of electricity (COE) reduction versus CO_2 permeance and CO_2/N_2 selectivity of membranes.

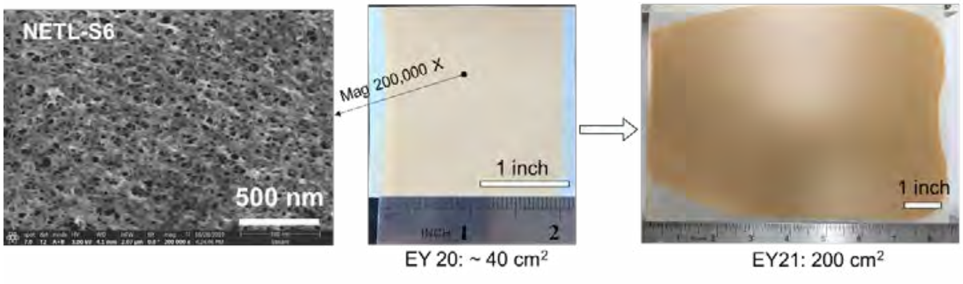

Figure 2: Surface micrograph of NETL-S6 membrane support and timeline of the evolving membrane support fabrication capabilities.

NETL-RIC has developed and optimized rubbery polymer blends (P15 polymers) having excellent CO_2/N_2 separation performance that exceeds Robeson's 2008 upper bound limit (Figure 3). This series of polymer blends are completely rubbery, so they are resistant to physical aging. More importantly, the blends presented excellent thin-film formation ability. Figure 3 also shows a general scheme of transforming a bulk material into a functioning TFC membrane via film thickness reduction. The TFC membranes consist of a top thin selective layer and a gutter layer made of polydimethylsiloxane (PDMS), which are both appended to the aforementioned NETL-S6 membrane support. As shown in Figure 4, small TFC membrane coupons (<10 cm^2) have shown CO_2/N_2 separation performance beyond the project target.

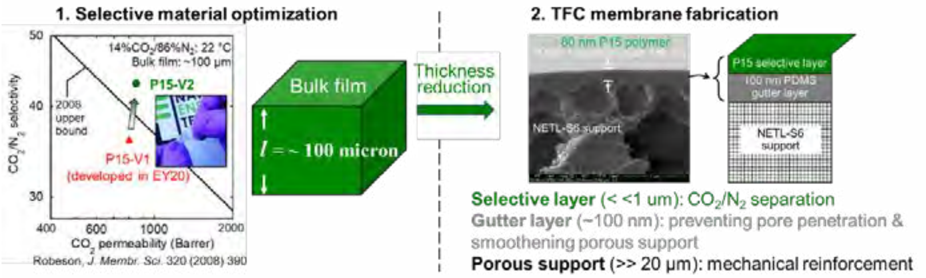

Figure 3: Selective layer material optimization and TFC development.

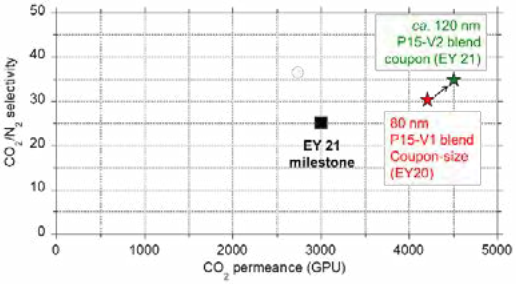

Figure 4: Comparison of CO_2/N_2 separation performance of the fabricated polymer blend TFC membranes with the target performance.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymer	
Materials of Fabrication for Support Layer	—	Proprietary polymer	
Nominal Thickness of Selective Layer	μm	0.1 – 0.4	0.1 – 0.4
Membrane Geometry	—	flat-sheet	flat-sheet
Max Trans-Membrane Pressure	bar	>4	>4
Hours Tested without Significant Degradation	—	N/A	500 hours
Manufacturing Cost for Membrane Material	$/m^2	N/A	N/A
Membrane Performance			
Temperature	°C	20 – 60	20 – 60
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000 – 4,500	3,000
CO_2/H_2O Selectivity	—	N/A	N/A
CO_2/N_2 Selectivity	—	20 –35	25
CO_2/SO_2 Selectivity	—	N/A	N/A
Type of Measurement	—	Pure gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Crossflow and countercurrent in plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	vacuum permeate	
Flue Gas Flowrate	SLPM	6	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% >95% 140	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/m/permeate: <0.01/m	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

***Flow Arrangement* –** Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

***Packing Density* –** Ratio of the active surface area of the membrane to the volume of the module.

***Shell-Side Fluid* –** Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- High-permeance TFC membranes.
- High-porosity membrane supports have negligible resistance to gas transport.
- Resistant to physical aging, providing performance stability.
- High molecular weight blended polymers lead to excellent thin film (~100 nm) formation.
- Stable under high humidity conditions.
- Low cost compared to conventional amine absorption.

R&D challenges

- Scaling up polymer synthesis of the selective layer materials.
- Fabricating ultra-thin, defect-free membranes in large areas.
- Maintaining robust performance in the long term under harsh operating conditions with high humidity, acid gases (sulfur oxide [SO_X] and nitrogen oxide [NO_X]), and other trace contaminants, such as flue ash, mercury (Hg), etc.

available reports/technical papers

Keairns, D.; Fout, T.; Hopkinson, D., 2022, “A cost and performance analysis of polymeric membrane-based post-combustion carbon capture,” (in pre-publication and to be submitted to Journal of Membrane Science).

Zhu, L.; Kusuma, V.; Hopkinson, D., “Highly Permeable Thin Film Composite Membranes of Rubbery Polymer Blends for CO_2 Capture.” 2021 DOE/NETL Carbon Management and Oil & Gas Research Project Review Meeting. Point Source Carbon Capture – Lab, Bench, and Pilot-Scale Research. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Zhu.pdf*.

Microporous Polymeric Sorbent Technology for Post-Combustion CO_2 Capture

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Shapeable Microporous Polymeric Sorbent

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
FWP-1022402 (Task 17)

predecessor project:
2020 Carbon Capture FWP

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partners:
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primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new, microporous polymeric (m-poly) sorbent technology with a demonstrated carbon dioxide (CO_2) uptake capacity of 10 wt% and a selectivity of greater than 500 under a "simulated gas" environment for natural gas flue gas (NGFG). The most promising m-poly sorbents are to be integrated into a prototype modular system for long-term field testing (such as at the National Carbon Capture Center [NCCC]) under actual post-combustion flue gas.

technical goals

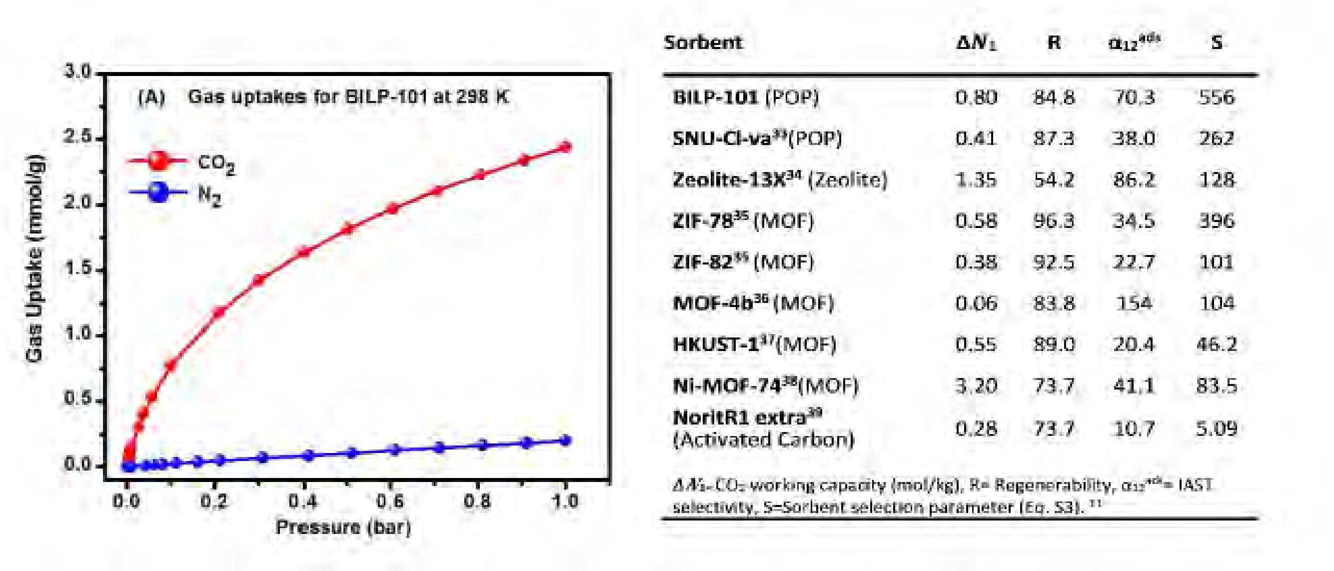
- Identify a sorbent material with a potential of achieving a CO_2 uptake property of 7 wt% and a CO_2/Nitrogen (N_2) selectivity of 500. Evaluate materials under NGFG environments.
- Demonstrate the sorbent material in fiber form with a potential of achieving a CO_2 uptake property of 7 wt% and a CO_2 selectivity of 500. Evaluate the fiber materials under neat environments.
- Test a sorbent prototype under simulated or actual NGFG.
- Perform a techno-economic analysis (TEA) with experimental data to calculate the cost of achieving 95% capture efficiency (conducted by Strategic Systems Analysis and Engineering [SSAE] team).

technical content

The selective removal of CO_2 from dilute, mixed gas streams at the scales associated with centralized power generation represents a significant challenge. Adding to this challenge is the need to rapidly develop and deploy a separation technology that delivers a viable option in the next few years with the delivered technology also having minimal impact on the delivered cost of electricity (COE) to the customer. Sorbent materials have been studied intensively in recent years for CO_2 capture. Inorganic sorbents, such as aminated silica and metal organic frameworks (MOFs), showed significant CO_2 capture performance. However, chemical stability, amine leaching, high regeneration temperature, slow sorption kinetics, and poor cyclability have been major drawbacks for these sorbents. On the other hand, polymeric sorbents, such as porous polymeric networks (PPNs) and benzimidazole linked polymers (BILPs), have been developed with high chemical stability and fast adsorption/desorption cycles. In general, porous polymers suffer from use of costly monomers/reactants, harsh synthesis conditions, and lower CO_2 capture capacity compared to their inorganic counterparts.

The removal of CO_2 from natural gas combined cycle (NGCC), as compared to coal-derived flue gas (pulverized coal), can be considered even more challenging. Carbon dioxide is present at lower levels (~4 vol% versus >12 vol%), representing less partial pressure driving force available for separation. Oxygen (O_2) is significantly higher (~12 vol% versus 3 vol%), necessitating that the sorbent possesses oxidative stability, a valid concern for amine-based materials. Moisture is lower for NGCC flue gas (~8 vol%) versus pulverized coal flue gas (~14 vol%), but can still include the difficulty of competitive adsorption of H_2O being favored over CO_2. There is a need for high CO_2 capacity sorbents that are chemically stable, inexpensive, and have a simple synthesis procedure.

Over the past several years, NETL has provided the foundational knowledge and technology progress that can overcome the challenges associated with the maturation of polymer-based sorbent technology. For example, NETL has developed BILPs demonstrating the highest CO_2 uptake and CO_2/N_2 selectivity of all other PBIs reported to date (Figure 1). Low-temperature CO_2 regeneration, fast kinetics, and high chemical stability all combine to make this sorbent a promising candidate for carbon capture (Figure 1). The team recently developed a soluble m-poly functionalized with carboxylic acid groups. Functionalized polymers were impregnated with alkyl amines that formed a stable sorbent. These polymers showed high CO_2 uptake and CO_2/N_2 selectivity, which is more than four times higher compared to similar sorbents. Sorbents tested under humid conditions showed chemical stability and the CO_2 uptake performance remained intact after several cycles. Moreover, these sorbents were able to be regenerated at 85°C.



Sorbent	ΔN_1	R	α_{12}^{ads}	S
BILP-101 (POP)	0.80	84.8	70.3	556
SNU-Cl-va[33](POP)	0.41	87.3	38.0	262
Zeolite-13X[34] (Zeolite)	1.35	54.2	86.2	128
ZIF-78[35] (MOF)	0.58	96.3	34.5	396
ZIF-82[35] (MOF)	0.38	92.5	22.7	101
MOF-4b[36] (MOF)	0.06	83.8	154	104
HKUST-1[37](MOF)	0.55	89.0	20.4	46.2
Ni-MOF-74[38](MOF)	3.20	73.7	41.1	83.5
NoritR1 extra[39] (Activated Carbon)	0.28	73.7	10.7	5.09

ΔN_1-CO_2 working capacity (mol/kg), R= Regenerability, α_{12}^{ads}= IAST selectivity, S=Sorbent selection parameter (Eq. S3).[11]

Figure 1: CO_2 and N_2 adsorption isotherm of the BILP sorbent and the list of top-performing sorbents for flue gas (CO_2/N_2:10/90) separation using vacuum swing adsorption at 298K, P_{ads}=1 bar, and P_{des}=0.1 bar.

In the first phase, several proposed polymeric sorbents were developed. Specifically, the sorbent series PIM-1-AO-DETA (Figure 2) showed high CO_2 uptake capacity (Figure 3) and CO_2/N_2 selectivity, exceeding the 7 wt% CO_2 uptake milestones of the first year. Carbon dioxide uptake capacity of sorbents remains intact in humid conditions after several regeneration cycles (Figure 4). As-synthesized sorbents were characterized and scaled up to be processed into fibers in the second year.

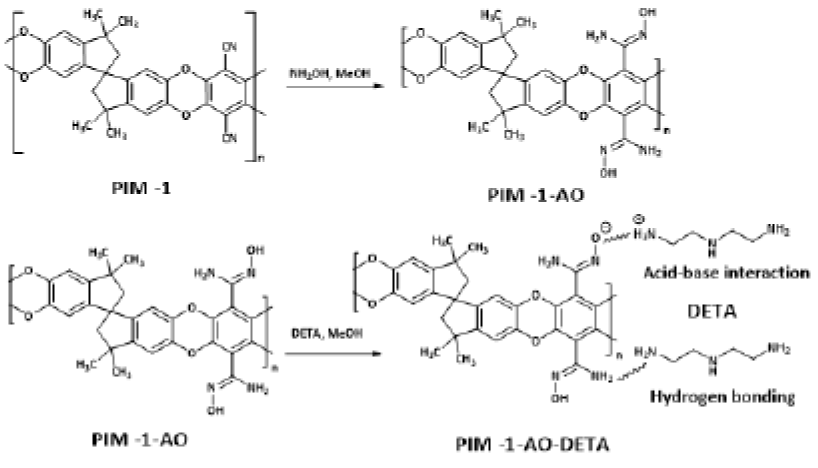


Figure 2: Reaction scheme and preparation of PIM-1-AO-DETA sorbent.

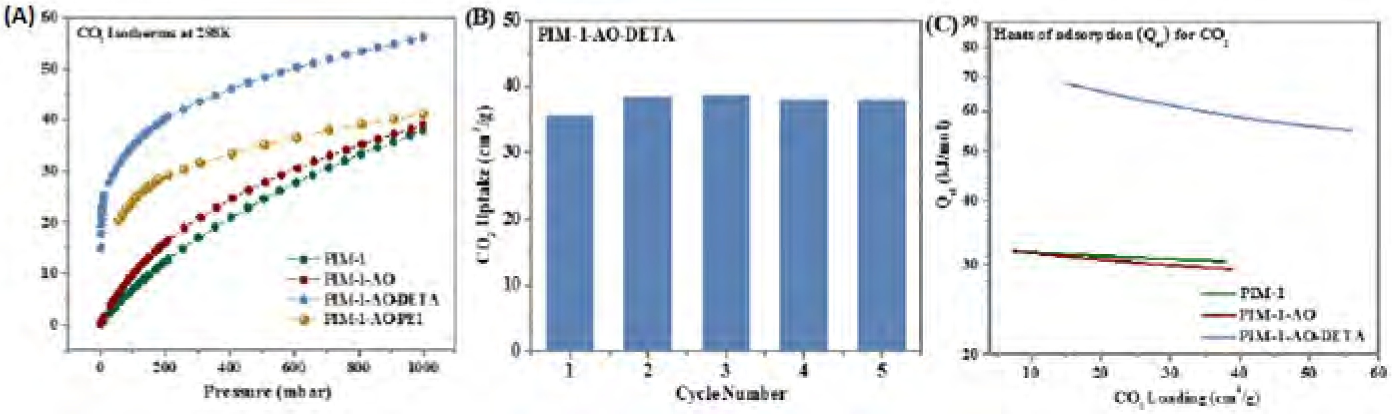


Figure 3: (A) CO_2 uptake isotherm of the discovered sorbent (PIM-1-AO-DETA) in comparison with neat PIM-1, functionalized (PIM-1-AO), and PEI impregnated PIM-1 (PIM-1-PEI). (B) CO_2 cyclability of PIM-1-AO-DETA (regenerated only at 80°C). (C) Heat of adsorption for CO_2 for the sorbents.

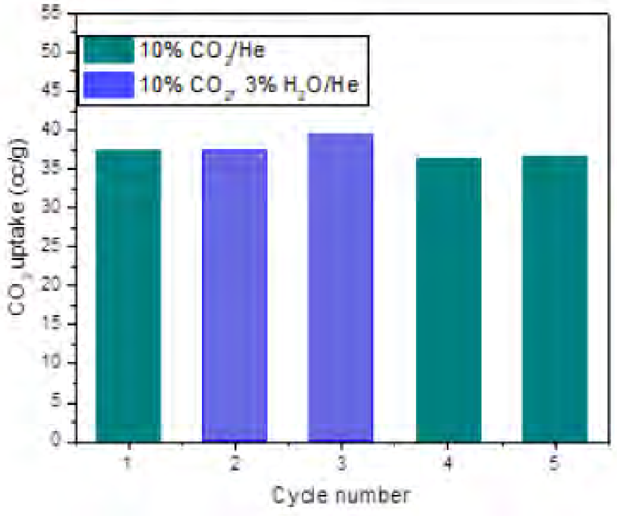


Figure 4: Preliminary CO_2 uptake performance of NETL's high-performance m-poly-1 tested in packed-bed reactor with gas breakthrough analysis under dry and humid conditions.

Continued work is being directed toward the development of new m-poly sorbents. The major advantage of m-poly over other porous materials, such as MOFs and zeolites, is very high chemical stability because of the strong covalent bond linking the polymer backbone. Unlike previous work with BILPs, these sorbents are being structured from contorted one-dimensional monomers, which provide sorbent solubility in common solvents. In the case of other sorbents, such as BILPs, MOFs, silica, and zeolites, they need to be processed with other additives, which usually causes a large decrease in their CO_2 uptake capacity. On the other hand, the proposed m-poly sorbents can be processed into desired sorbent shapes such as pellets, beads, fibers, etc., depending on the reactor design configuration envisioned for the capture process.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	1.1	—
Average Particle Diameter	mm	1	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	0.1	—
Temperature	°C	25	—
Equilibrium Loading	g mol CO_2/kg	2.1	—
Heat of Adsorption	kJ/mol CO_2	47	—
Desorption			
Pressure	bar	1	—
Temperature	°C	75	—
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical structure of the sorbent consist of porous polymer with amidoxime and alkylamines functionalities.

Sorbent Contaminant Resistance – Sorbent is stable through humidity, sulfur oxide (SO_X), and nitrogen oxide (NO_X).

Sorbent Attrition and Thermal/Hydrothermal Stability – 200°C.

technology advantages

- M-poly sorbent technology has small footprint, simplicity of device and process, ease of operation, modularity, and low parasitic energy requirements through low-temperature desorption (<85°C) to remove all adsorbed gases.
- The m-poly sorbent has high surface area, permanent microporosity, functionable structure, uniform pore size distribution, and high chemical and thermal stability, helping to address the challenges facing carbon capture from centralized point sources.
- Carbon dioxide uptake capacity of sorbents remains intact in humid conditions after several regeneration cycles.
- In contrast to other sorbents, soluble m-poly can be dissolved in common solvents and processed into the desired shape without any other material.

R&D challenges

- There is a lack of polymer functionalization study and a lack of a detailed processability study to transfer technology to market.

available reports/technical papers

Ali K. Sekizkardes, Sonia Hammache, James S. Hoffman, Polymers of Intrinsic Microporosity Chemical Sorbents Utilizing Primary Amine Appendance Through Acid–Base and Hydrogen-Bonding Interactions, David Hopkinson, ACS Appl. Mater. Interfaces 2019, 11, 34, 30987–30991, *https://doi.org/10.1021/acsami.9b09856*.

D. Hopkinson, A.K. Sekizkardes, Polymer for carbon dioxide capture and separation, U.S. Department of Energy, USA Patent no 10,323,125. 2019, pp. 22 *https://www.osti.gov/servlets/purl/1568476*.

A. Miles, W.C. Wilfong, D. Hopkinson, A.K. Sekizkardes, Alkylamine Incorporation in Amidoxime Functionalized Polymers of Intrinsic Microporosity for Gas Capture and Separation, Energy Technol. (Weinheim, Ger.), 8 (2020) 2000419. *https://doi.org/10.1002/ente.202000419*.

A.K. Sekizkardes, V.A. Kusuma, J.T. Culp, P. Muldoon, J. Hoffman, D. Hopkinson, Single polymer sorbent fibers for high performance and rapid direct air capture, ChemRxiv, (2022) 1-4. *https://doi.org/10.26434/chemrxiv-2022-jgpqv*.

Hybrid Solvent-Membrane Process for Pre-Combustion CO_2 Capture

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is assessing the potential of integrating small-scale modular pre-combustion carbon dioxide (CO_2) capture processes with small-scale modular coal gasification technologies. The research is focused on the development of a hybrid process combining hydrogen (H_2)-selective membranes followed by solvent capture for CO_2. NETL-RIC is developing an H_2-selective cross-linked polyamide nanofilm-based composite membrane for upstream CO_2 capture. NETL-RIC is also investigating the corrosion rates in carbon and stainless steels from solvent-based pre-combustion carbon capture processes.

technical goals

H_2-Selective Membranes

- Optimize a polymeric porous membrane support and polydimethylsiloxane (PDMS) gutter layer for the formation of an H_2-selective polyamide nanofilm for H_2/CO_2 separation at high temperatures.

CO_2-Selective Solvents

- Perform corrosion rate measurements for aqueous solutions and hydrophobic physical solvents under variable conditions of CO_2 partial pressure and temperature.
- Provide corrosion control strategies to process scale-up and materials.

technical content

Transitioning from traditional gasification technologies to more flexible and modular gasification processes will enable the use of alternative and cheaper local feedstocks (e.g., low-quality coal, biomass, and municipal solid waste), which will result in syngas of varying components and composition. Integrating small-scale, modular pre-combustion carbon capture systems with modular gasification offers the opportunity for cost reduction of novel capture processes through mass production of smaller capture units and learning curve effects. However, there is a need to identify carbon capture technologies that demonstrate advantages at a smaller, modular scale, as a traditional solvent-only absorption process (e.g., Selexol) may have a cost disadvantage at modular gasification scales. The results of a gap analysis and literature review ("*Modular CO_2 Capture Processes for Integration with Modular Scale Gasification Technologies: Literature Review and Gap Analysis for Future R&D*" – listed under available reports/technical papers/presentations) assessing the potential for modular carbon capture technologies to be applied to a variety of gasification products determined that H_2-selective membranes followed by solvent capture for CO_2 is promising for several modular-scale gasification processes and multiple product areas, such as electricity, H_2, and ammonia production. The use of hybrid capture processes can enhance the overall capture performance at modular scale, as the presence of one unit can mitigate the shortcomings of the other. Additionally, hybrid systems have lower capital and operating costs, are flexible in handling changes in feed

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Hybrid

project focus:
Solvent-Membrane Process Applied to Modular-Scale Pre-Combustion CO_2 Capture

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
FWP-1022402 (Tasks 14,15)

predecessor project:
2020 Carbon Capture FWP

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partners:
University of North Dakota's Energy and Environmental Research Center; Carbon Capture Scientific LLC

gas conditions, and can allow the recycle of streams back to the water-gas shift (WGS) system. Under flexible, small-scale conditions, there is also the potential for partial carbon capture at the module's capacity, which could be increased as needed with the addition of more modules that have demonstrated successful operation. Appropriately sized modular units for partial carbon capture could significantly reduce energy costs by using available waste heat.

H_2-Selective Membranes

Cross-linked polyamide membranes consist of a bottom porous support layer, an intermediate gutter layer, and a top polyamide selective layer (or polyamide nanofilm). The three components are being designed and developed dependently, as the physical and gas transport properties of each layer are greatly affected by the layer beneath it. The polyamide layer provides effective base H_2/CO_2 separation properties, while the porous support and gutter layer provide reinforcement without adding significant mass transfer resistance to the polyamide layer. The current reported cross-linked polyamide membrane exhibits H_2 permeance of 350 gas permeation units (GPU) and H_2/CO_2 selectivity of 50 at 140°C; however, the membrane was fabricated via traditional interfacial polymerization, through which the polyamide layer is 100–300 nm thick, with a wrinkled, ridge-and-valley structure. The aim of this project is to fabricate thinner sub-50 nm polyamide nanofilms via an improved interfacial polymerization approach to effectively boost H_2 permeance of the membranes.

NETL is fabricating functioning polyamide thin-film composite (TFC) membranes for high-temperature H_2/CO_2 separation with the following approach (Figure 1): (1) fabricating a porous support thermally stable at 100–250°C, (2) coating a highly permeable PDMS gutter layer, (3) functioning the PDMS surface with amine groups, and (4) fabricating a highly cross-linked polyamide nanofilm on the amine-PDMS surface via precisely controlled interfacial polymerization. In this approach, the porous support's pore size, surface porosity, gutter layer thickness, and amine functionality can be tailored according to the resulting polyamide layer properties, with a goal of achieving defect-free polyamide as thin as possible. Screening tests performed in a mixed gas feed of 50% H_2/50% CO_2 are being used to identify the best-performing polyamide nanofilms (a target performance of H_2 permeance of ≥600 GPU and H_2/CO_2 selectivity ≥30 at 100–250°C) to be further evaluated with real shifted syngas. Note that the highest H_2/CO_2 permeance selectivity at room temperature was found to be 26 based on the literature survey of about 1,600 sets of different gas permeabilities in approximately 800 different polymers.

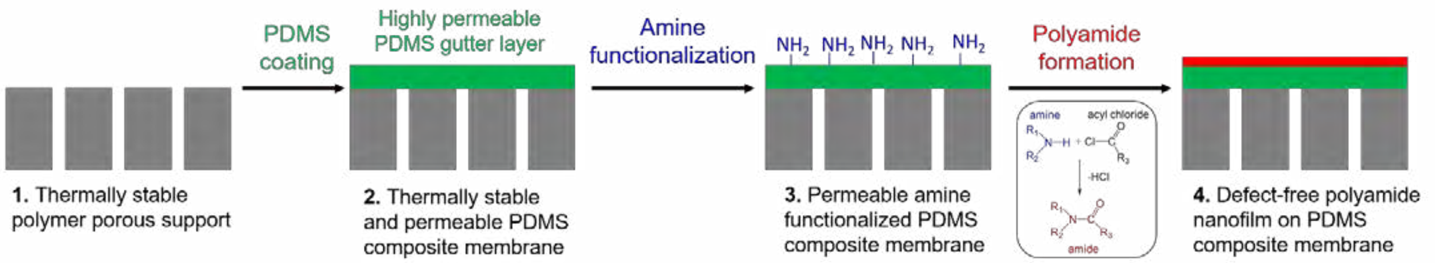


Figure 1: Preparation steps for a cross-linked polyamide nanofilm on a PDMS composite membrane.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Cross-linked polyamide	
Materials of Fabrication for Support Layer	—	Polymer/non-woven fabric	
Nominal Thickness of Selective Layer	µm	≤0.05	≤0.05
Membrane Geometry	—	Flat-sheet	Flat-sheet
Maximum Trans-Membrane Pressure	bar	—	—
Hours Tested without Significant Degradation	—	—	720
Manufacturing Cost for Membrane Material	$/m^2	—	—
Membrane Performance			
Temperature	°C	150	100-250
H_2 Pressure Normalized Flux	GPU or equivalent	350	600
H_2/H_2O Selectivity	—	—	—
H_2/CO_2 Selectivity	—	38	30
H_2/H_2S Selectivity	—	—	—
Sulfur Tolerance	ppm	—	—
Type of Measurement	—	Pure-gas	Mixed-gas
Proposed Module Design			
Flow Arrangement	—	Spiral wound or plate-and-frame	
Packing Density	m^2/m^3	—	
Shell-Side Fluid	—	—	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
H_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (STP, 1 atm, 0°C ideal gas)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-10} mol/m^2-s-Pa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be used for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Selective layer materials employ the solution-diffusion mechanism to separate gas molecules and the driving forces are partial pressure differences across the membrane.

Contaminant Resistance – Not yet available.

Syngas Pretreatment Requirements – Not yet available.

Membrane Replacement Requirements – Not yet available.

Waste Streams Generated – Not yet available.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

Proposed Module Design – Spiral wound or plate-and-frame. Note the module location, as well as the pressure, temperature, and composition of the gas entering the module.

CO_2-Selective Solvents

NETL-RIC is investigating the corrosion rates of steel alloys used in pre-combustion carbon capture process equipment in the presence of high-pressure CO_2, H_2, water, and capture solvents. While extensive studies have been performed to understand CO_2 corrosion mechanisms on carbon steel in different applications, such as amine-based CO_2 capture for post-combustion, natural gas transportation, and ultra-deep drilling, there is a lack of published data on corrosion rates of steel in pre-combustion CO_2 capture processes. With a better understanding of the corrosion mechanism in different physical solvents, corrosion control strategies can be proposed for process design and material development. The selection of optimal materials for piping, vessels, and all types of equipment is vital in ensuring the long-term performance and safety assertion of the capture plants through their lifetime. For instance, the levelized cost of capture (LCOC) for pre-combustion capture solvents could be reduced by up to 10% using carbon steel versus stainless steels, corresponding to a lifetime cost savings of up to $80M at a 550-megawatt-electric (MWe)-scale power plant.

The project focus is on quantifying the corrosion rate and products to determine the corrosion mechanism experienced by carbon and stainless steel alloys in the presence of both commercial and NETL-RIC-developed solvents.

Carbon dioxide that is dissolved into water can react to form carbonic acid (H_2CO_3), which can corrode steel equipment through the reaction:

$$Fe(s)+H_2CO_3(aq)\rightarrow FeCO_3(s/aq)+H_2(g)$$

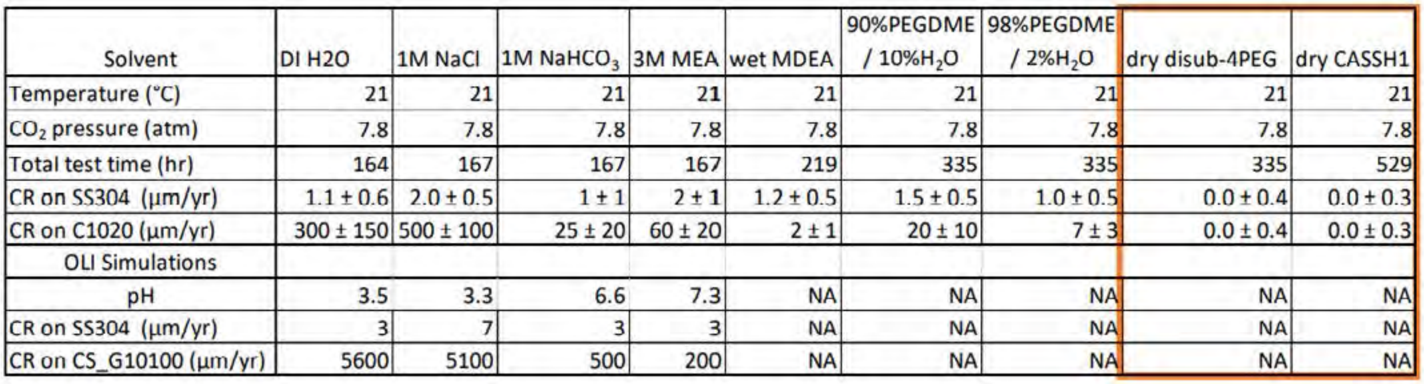
The generation of solid ferrous carbonate ($FeCO_3$) versus dissolved $FeCO_3$ is highly affected by environmental factors, including temperature, water concentration, CO_2 partial pressure, flowrate, and time. Corrosion by hydrogen sulfide (H_2S) can also occur in pre-combustion capture processes due to H_2 consuming the iron oxide passivation layer, which can increase the corrosion rate. Therefore, it is important to measure corrosion in the presence of CO_2 and H_2.

Current commercial pre-combustion solvents, such as Selexol, are hydrophilic and tend to absorb substantial amounts of water, which, in the presence of CO_2, can provide conditions that are conducive to corrosion of the metal. Solvents with high corrosion rates require thicker vessel walls, which can cause large upfront capital costs and could lead to undesirable down time for repairs to corroded elements in the capture system. Previous research at NETL has led to hydrophobic solvents (e.g., CASSH-1) that absorb minimal amounts of moisture, and which are expected to support far less corrosion under realistic carbon capture conditions.

A series of tests are being conducted to measure corrosion rates of two types of steel coupons (Carbon Steel C1020 and Stainless Steel SS304), with various commercial pre-combustion capture solvents and NETL-developed hydrophobic solvents, in the presence of pure CO_2 and under simulated syngas conditions (50% CO_2/50% H_2). The steel coupons are submerged for a period of one week to one month in a Parr reactor vessel under pressurized conditions of CO_2. Corrosion rates are then quantified by two methods: using the weight loss measurements of the coupons (gravimetric method) and by measuring the dissolved metals content in the post-test aqueous solutions. Table 2 shows that the corrosion rates for two NETL-patented solvents (dry disub-4PEG and CASSH-1) were below the detection limit after testing for more than 335 hours, indicating superior corrosion resistance compared with the other solvents tested, even for carbon steel. Tests are also being performed under varying temperatures, with the partial pressure of CO_2 adjusted to maintain constant CO_2 uptake, to determine the effect of temperature on the corrosion rate.

Computational simulations of the corrosion mechanisms are being performed using commercial software (OLI Studio) and the predicted rates of corrosion are being compared to the experimental data.

TABLE 2: EXPERIMENTAL AND SIMULATED CORROSION RATES IN BASELINE AQUEOUS AND PRE-COMBUSTION CO_2 CAPTURE PHYSICAL SOLVENTS



Solvent	DI H2O	1M NaCl	1M $NaHCO_3$	3M MEA	wet MDEA	90%PEGDME / 10%H_2O	98%PEGDME / 2%H_2O	dry disub-4PEG	dry CASSH1
Temperature (°C)	21	21	21	21	21	21	21	21	21
CO_2 pressure (atm)	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Total test time (hr)	164	167	167	167	219	335	335	335	529
CR on SS304 (µm/yr)	1.1 ± 0.6	2.0 ± 0.5	1 ± 1	2 ± 1	1.2 ± 0.5	1.5 ± 0.5	1.0 ± 0.5	0.0 ± 0.4	0.0 ± 0.3
CR on C1020 (µm/yr)	300 ± 150	500 ± 100	25 ± 20	60 ± 20	2 ± 1	20 ± 10	7 ± 3	0.0 ± 0.4	0.0 ± 0.3
OLI Simulations									
pH	3.5	3.3	6.6	7.3	NA	NA	NA	NA	NA
CR on SS304 (µm/yr)	3	7	3	3	NA	NA	NA	NA	NA
CR on CS_G10100 (µm/yr)	5600	5100	500	200	NA	NA	NA	NA	NA

Note: Corrosion rates shown were calculated by gravimetric method for two different types of steel.

technology advantages

- The combination of H_2-selective membranes with CO_2-selective solvents creates an efficient and size-reduced process that is ideal for modular gasification scales.
- Integrating small-scale, modular pre-combustion carbon capture systems with modular gasification offers the opportunity for cost reduction of novel capture processes through mass production of smaller capture systems.
- The modular-scale pre-combustion capture process developed in this project will also be relevant to H_2 generation from steam methane reforming applications.
- NETL has existing subcontracts or collaborations with two major modular gasification research centers—the University of North Dakota's Environmental Research Center (UNDEERC) and the University of Kentucky's Center for Applied Energy Research (UK-CAER).

R&D challenges

- Developing a polyamide nanofilm composite membrane that is thermally stable at elevated temperatures of 100–250°C and achieves H_2 permeance of greater than or equal to 600 GPU and H_2/CO_2 selectivity greater than or equal to 30.
- Obtaining corrosion rate measurements under pre-combustion CO_2 capture conditions is challenging due to the capture of CO_2 occurring at relatively high pressure.
- Long exposure time is required to obtain repeatable and reliable corrosion rates, as they tend to be high initially before reaching a steady state.
- Obtaining corrosion rates in the presence of H_2S requires significant safety processes to manage any possible leak of H_2S.
- Temperature and CO_2 partial pressure can affect the CO_2 corrosion rate by affecting the uptake of CO_2 into the solvent.
- Water concentration in solvents can affect the rate and extent of corrosion, especially under acidic conditions.

status

A polymer porous support was successfully fabricated via a phase inversion technique and a series of laboratory-scale PDMS gutter layer membrane coupons were fabricated on top of the porous supports. The thermal stability of the polymer porous supports was evaluated by comparing the gas permeances before and after thermal treatments at 100–200°C for two to 24 hours. The treatments had no significant effect on gas permeances, and the optimized porous supports showed a pure-gas H_2 permeance greater than 60,000 GPU. The H_2 and CO_2 permeances and physical aging behaviors of the PDMS gutter layer membrane coupons were investigated at 25–150°C, resulting in no significant physical aging (<10% permeance reduction) over the course of 1,152 hours (48 days). Based on the developed PDMS gutter layer membranes, 11 polyamide nanofilm coupons were fabricated and tested for H_2/CO_2 separation at 25–150°C. The best sample showed H_2 permeance of 350 GPU and H_2/CO_2 selectivity of 38 at 150°C. The polyamide nanofilm is undergoing testing at temperatures greater than 150°C with the goal of increasing H_2 permeance. Machine learning techniques are being used for computational screening of polymers for H_2/CO_2 separation. The screening protocol allows for the down-selection of materials, so that the top 10 polymer precursor materials with the desired free volume characteristics, high permeability and selectivity, and tolerance to contaminants (e.g., sulfur) for selective hydrogen separations are selected for generating carbon molecular sieve (CMS) membranes.

Corrosion rates were measured in carbon steel and stainless steel for eight different solvents and aqueous solutions in the presence of pure CO_2 and mixed gas composition of 50% CO_2/50% H_2 at two different pressure conditions (100 and 400 pounds per square inch gauge [psig]) and temperature conditions (21 and 40°C). Corrosion rates and solution speciation were simulated by OLI Studio software and compared well with experimental data for stainless steels.

available reports/technical papers/presentations

Zhu, L. and Hopkinson, D., “High Performance Thin Film Composite Membranes for Post Combustion Carbon Capture,” DOE-NETL’s 2020 Integrated Project Review Meeting-Carbon Capture, Pittsburgh, PA (2020). *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Zhu.pdf*.

Siefert, N., “Low Corrosion Pre-Combustion Solvents for Novel Solvent/Membrane Hybrid Capture Processes,” DOE-NETL’s 2021 Carbon Management and Oil and Gas Research Project Review Meeting – Point Source Capture (2021). *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Siefert.pdf*.

Shi, W., Tiwari, S., Thompson, R., Culp, J., Hong, L., Hopkinson, D., Smith, K., Resnik, K., Steckel, J., Siefert, S., “Computational Screening of Physical Solvents for CO_2 Pre-combustion Capture.” The Journal of Physical Chemistry B 125 (49), 13467-13481. *https://pubs.acs.org/doi/abs/10.1021/acs.jpcb.1c07268*.

Hopkinson, D., Siefert, N., Thompson, R., Macala, M., Hong, L., “Di-substituted siloxane solvents for gas capture.” US Patent 10,589,228. *https://patents.google.com/patent/US10589228B2/en*.

Smith, K.; Chen, S.; Siefert, N. “Modular CO_2 Capture Processes for Integration with Modular Scale Gasification Technologies: Literature Review and Gap Analysis for Future R&D”; DOE/NETL-2020.2149; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Pittsburgh, PA, 2020; p 136. DOI: 10.2172/1668758. *https://edx.netl.doe.gov/dataset/modular-co2-capture-processes-for-integration-w-modular-scale-gasification-technologies*

Hollow Fiber Chemisorption Sorbent

primary project goal

The project objective is to provide a viable basic immobilized amine sorbent (BIAS)-based hollow chemisorption fiber sorbent (hollow-CHEFS) demonstrating carbon dioxide (CO_2) capture in diluted environments with a concentration near 400 parts per million (ppm). The hollow-CHEFS target is to achieve a 0.3 mmol CO_2/g capacity that is highly stable over at least three adsorption-desorption cycles. The resulting data will be used to complete a techno-economic analysis (TEA) to evaluate the feasibility of a rapid temperature swing adsorption (RTSA) process using the hollow-CHEFS.

technical goals

- Achieve a CO_2 capture of 0.3 mmol CO_2/g-fiber from simulated air by CHEFS and demonstrate at least three adsorption-desorption cycles.
- Complete a pre-screening analysis for a CHEFS-based rapid temperature swing CO_2 adsorption system.
- Scale-up hollow-CHEFS fabrication and incorporate into a two-fiber module that will be used to evaluate CO_2 capture under ambient air environments.

technical content

Direct air capture (DAC) removes CO_2 directly from the air and is an alternate complementary technology to the capture of CO_2 from large point sources. DAC has the advantage of addressing CO_2 emissions from all sources, including mobile sources, if the technology is operated on a sufficiently large scale. However, air capture presents the technical challenge of developing adsorbents that operate under near-ambient conditions and can extract CO_2 from ultra-dilute sources, 200–600 ppm in concentration. Silica-modified BIASs are promising materials for CO_2 capture from ultra-diluted gas steams such as ambient air. However, a typical BIAS suffers low mechanical strength, low and inefficient heat transfer through a solid bed, and hydrothermal degradation/amine leaching by water vapor.

Over the past few years, the National Energy Technology Laboratory (NETL) has provided the foundational knowledge and technology progress that overcomes the challenges associated with the maturation of BIAS design and application. These include (1) a crosslinked BIAS designed for high stability to water vapor; (2) outstanding CO_2 capture capacity from ambient air; (3) easy scale-up—commercial partner has made 18 kg sorbent at pilot scale; and (4) low energy cost and low waste production for material manufacture and operation. NETL has hollow fiber fabrication and test systems ready for BIAS-based hollow-CHEFS screening. NETL previously (1) synthesized a crosslinked BIAS resistant to organics leaching by precursor fiber sorbent dope solvent; (2) fabricated solid-CHEFS and hollow-CHEFS (Figure 1) for the capture of CO_2; and (3) initiated a non-disclosure agreement (NDA) process with the Georgia Institute of Technology for fiber synthesis scale-up work. Compared to up-to-date literature for immobilized amine sorbent-based fibers, the stability of NETL's pre-functionalized crosslinked material affords a more homogeneous (even amine distribution) and more reliable fiber that is prepared faster and simpler than those prepared by post-infusion.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
CO_2 Capture from Air with Hollow Fiber Sorbents

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
FWP-1022402 (Task 18)

predecessor project:
2020 Carbon Capture FWP

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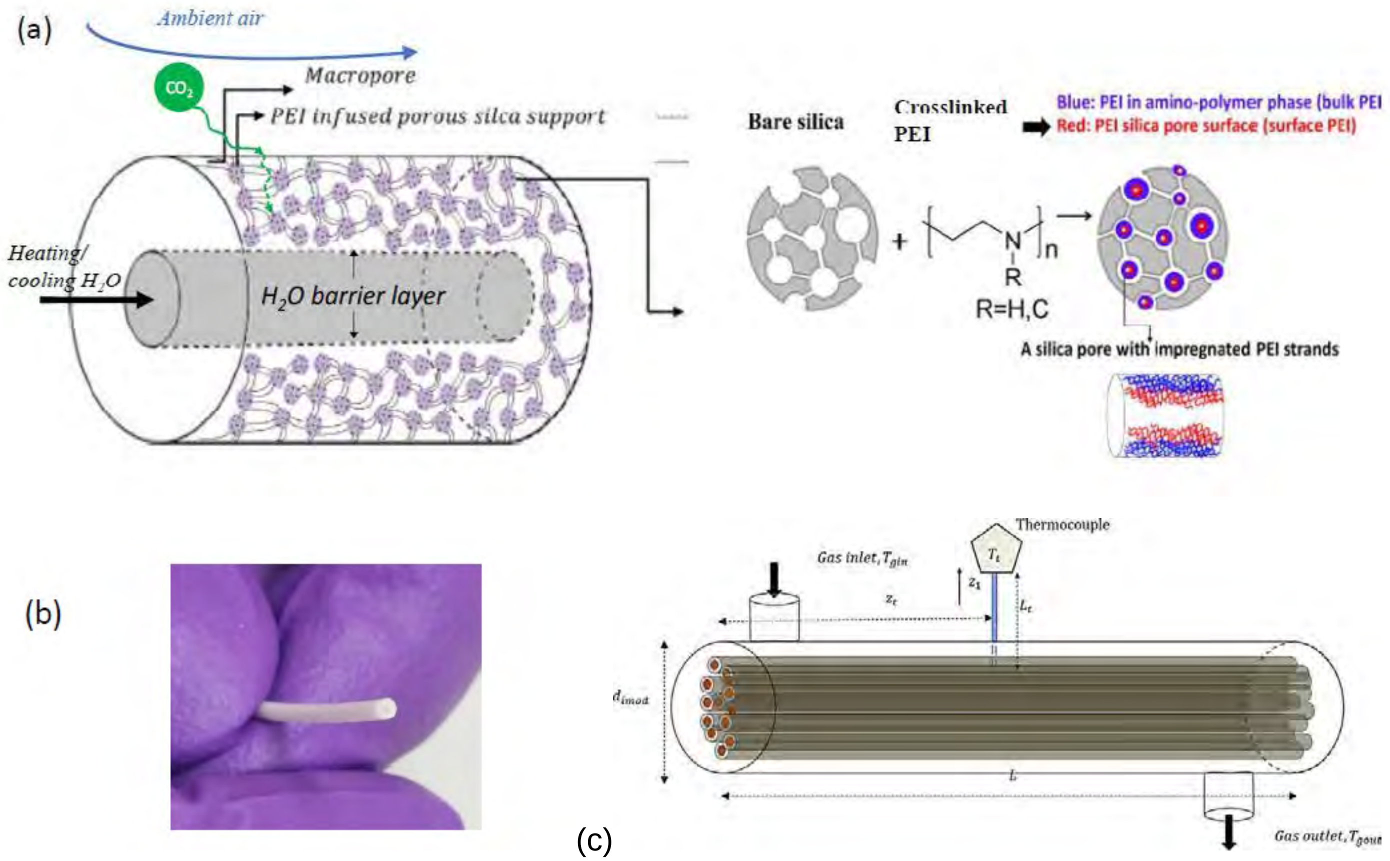

Figure 1: (a) General structure of the BIAS particles and envisioned test setup/CO_2 capture scheme for the hollow-CHEFS, (b) hollow-CHEFS photo image developed at NETL, and (c) schematic of a hollow-CHEFS membrane module[1].

In this project, the previously optimized BIAS is being incorporated into solid-CHEFS to rapidly define, screen, and optimize hollow-CHEFS components and performance. The hollow-CHEFS are complemented through a fabrication, characterization, and performance assessment for ambient air environments. Performance metrics and other information are being used to conduct a TEA of a system using CHEFS. The work is being pursued in two phases. Phase I, “Preliminary Hollow-CHEFS Fabrication and Optimization,” comprises the fabrication and characterization of hollow-CHEFS, as well as evaluation under neat environments. Phase II, “Hollow-CHEFS Fabrication Scale Up,” includes evaluating the feasibility of a hollow-CHEFS-based RTSA system for CO_2 capture under ambient air environments and scale-up hollow-CHEFS fabrication.

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[1] J. Kalyanaraman, Y. Fan, R.P. Lively, W.J. Koros, C.W. Jones, M.J. Realff, Y. Kawajiri, Modeling and experimental validation of carbon dioxide sorption on hollow fibers loaded with silica-supported poly(ethylenimine), Chem. Eng. J., 259 (2015) 737-751.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1.53	1.5
Bulk Density	kg/m^3	52	52
Average Particle Diameter	mm	NA	NA
Particle Void Fraction	m^3/m^3	NA	NA
Packing Density	m^3/m^3	0.165	<0.2
Solid Heat Capacity @ STP	kJ/kg-K	1.2	1.2
Crush Strength	kg_f	NA	—
Attrition Index	-	NA	—
Thermal Conductivity	W/(m-K)	NA	—
Manufacturing Cost for Sorbent	$/kg	TBD	TBD
Adsorption			
Pressure	bar	1	1
Temperature	°C	35	0-45
Equilibrium Loading	g mol CO_2/kg	0.26	>0.1
Heat of Adsorption	kJ/mol CO_2	32.7	<60
CO_2 Adsorption Kinetics	gmol/g*min	0.019	0.01-0.03
Desorption			
Pressure	bar	1	1
Temperature	°C	105	90-120
Equilibrium CO_2 Loading	g mol CO_2/kg	0.26	<0.1
Heat of Desorption	kJ/mol CO_2	NA	<60
CO_2 Desorption Kinetics	gmol/g*min	0.054	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Parallel	
Flue Gas Flowrate	kg/hr	NA	
Space Velocity	hr^{-1}	NA	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	0.0063	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90 >95%	1 bar
Adsorber Pressure Drop	bar	low	
Degradation	% capacity fade/cycle	0.0009%	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	NA	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	- °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Polyethylenimine (PEI) function groups on CHEFS provide chemisorption sites for CO_2 molecules, as shown in Figure 1(a).

Sorbent Contaminant Resistance – Sorbent stability has been reported in previous publications listed below.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent stability has been reported in previous publications listed below.

Flue Gas Pretreatment Requirements – TBD.

Sorbent Make-Up Requirements – TBD.

Waste Streams Generated – N/A.

technology advantages

- The NETL BIAS has shown outstanding performance that offers superior resistance to amine leaching based on a crosslinked amine network. A BIAS-based hollow-CHEFS offers high mechanical strength, low pressure drop, and efficient heat transfer for ambient air carbon capture.
- The hollow-CHEFS offer ease in collecting for transport and disposal and are easy to scale-up.
- Other key advantages over current CHEFS are (1) the fiber's superior stability imparted by the crosslinked amine-epoxy network of the BIAS within, and (2) a single-step spinning approach, where the preparation method avoids a post-amine infusion impregnation step because the stable BIASs are spun directly into the fiber and do not leach their amines.

R&D challenges

- Optimization of BIAS-based hollow-CHEFS composition for diluted CO_2 capture.
- Fabrication of composite hollow-CHEFS and the corresponding large-scale manufacturing.
- Optimization of device and process to fully exploit hollow-CHEFS technology advantages.
- Evaluation of hollow-CHEFS at scales and under environments needed to transfer technology to market.

status

After optimizing mechanical strength and the BIAS formulation recipe for hollow-fiber CHEFS, the project team successfully demonstrated CHEFS possessing a stable CO_2 capture capacity of greater than or equal to 0.3 mmol CO_2/g-fiber over three adsorption-desorption cycles. The optimal solid CHEFS formula is being prepared as a hollow-CHEFS for testing to acquire data for an RTSA process modeling effort. The new dual-layer hollow fiber sorbent concept is being designed for DAC with a lumen-layer polymer coating to act as a water barrier inside the fiber. The lumen layer coating can be performed with the newly spun CHEFS hollow fiber sorbents.

available reports/technical papers/presentations

Wilfong, W.C., et al., "Scale-Up of Immobilized Amine Sorbent Pellets for Landfill Gas Upgrading, Using Benchtop and Pilot Equipment," Powder Technology 395 (2022), 243-254.

Wilfong, W. C.; Kail, B. W.; Howard, B. H.; Wang, Q.; Shi, F.; Ji, T.; Gray, M. L., Steam-Stable Basic Immobilized Amine Sorbent Pellets for CO_2 Capture Under Practical Conditions. ACS Appl. Mater. Interfaces 2019.

Wilfong, W. C.; Kail, B. W.; Howard, B. H.; Fernandes de Aquino, T.; Teixeira Estevam, S.; Gray, M. L., Robust Immobilized Amine CO_2 Sorbent Pellets Utilizing a Poly(Chloroprene) Polymer Binder and Fly Ash Additive. Energy Technology 2017, 5 (2), 228-233.

Wilfong, W. C.; Kail, B. W.; Jones, C. W.; Pacheco, C.; Gray, M. L. Spectroscopic Investigation of the Mechanisms Responsible for the Superior Stability of Hybrid Class 1/Class 2 CO_2 Sorbents: A New Class 4 Category. ACS Appl. Mater. Interfaces 2016, 8 (20),12780-91.

Wilfong, W. C.; Gray, M. L.; Kail, B. W.; Howard, B. H., Pelletization of Immobilized Amine Carbon Dioxide Sorbents with Fly Ash and Poly(vinyl chloride). Energy Technology 2016, 4 (5), 610-619.

Wilfong, W. C.; Kail, B. W.; Gray, M. L., Rapid Screening of Immobilized Amine CO_2 Sorbents for Steam Stability by Their Direct Contact with Liquid H_2O. ChemSusChem 2015, 8 (12), 2041-5.

Coal-Based Nanoporous Sorbent

primary project goal

The project goal is to develop a sustainable and cost-efficient nanoporous sorbent derived from coal for direct air capture (DAC) of carbon dioxide (CO_2). The design of the sorbent involves the use of domestic coal converted into nanoporous CO_2-adsorbent material with high surface area and metal oxide functionalities.

technical goals

- Identify and synthesize a carbon sorbent material with the potential of achieving a CO_2 uptake of 4–7 wt% CO_2 from simulated air with a CO_2 concentration of 400 parts per million (ppm). Degradation target is below 5% under inert sweep gas conditions.
- Optimize sorbent formulation parameters and demonstrate CO_2 uptake of 7 wt% CO_2 in a multi-cycle test. Heat of adsorption target is 50–70 kilojoules (kJ)/mol.
- Downselect sorbent, scale-up the sorbent, and complete full gas adsorption and gas-breakthrough testing for simulated CO_2/air feed gas. Expected kinetics are 4–7 wt% CO_2 uptake and a degradation milestone below 10% over the cycles.

technical content

DAC has attracted ever-increasing interest due to its potential to contribute toward net-negative CO_2 emission goals. DAC faces major challenges with removing CO_2 from an ultra-dilute stream (~400 ppm CO_2 in air) and being more costly to separate CO_2 compared to more concentrated systems (like flue gases). Solid sorbents with strong CO_2 chemical binding are one of the main DAC technical approaches. Amine-based sorbents have been demonstrated in pilot plants (like Climeworks and Global Thermostat) but are challenged by massive CO_2 capture costs. Amine-functionalized adsorbents on porous solid supports such as zeolites, mesoporous silica, metal-organic frameworks (MOFs), and porous organic polymers (POPs) are intensively studied for flue gas. However, low CO_2 uptake, high sorbent cost, and long-term stability have been major drawbacks, along with inherent amine evaporation and oxidation. Overall, the sorbents for DAC are in their infancy. There is a need for new sorbents with desirable characteristics (i.e., high CO_2 adsorption capacity and stable performance in presence of water and oxygen) and new processes that can reduce CO_2 capture costs to achieve successful DAC. The National Energy Technology Laboratory (NETL) has been studying an extensive portfolio of coal conversions for clean energy and sorbents for CO_2 capture applications. The capability to create high surface area and adjust pore size in sorbents is a prime expertise that has developed over the years. Many porous adsorbents with high surface area and targeted functional groups to reach more efficient CO_2 capture have been developed.

Functionalization of porous sorbents with CO_2-attractive groups is an imperative task to enhance the CO_2 adsorption at very low concentrations. The project team is using low-cost domestic coals, which are suitable for generating novel nanoporous carbon sorbents with high surface area and porosity and functionalized metal oxides. The team creates high porosity (micro/mesoporous)

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Nanoporous CO_2 Sorbent Derived from Coal

participant:
National Energy Technology Laboratory–Research and Innovation Center

project number:
FWP-1022402 (Task 19)

predecessor project:
N/A

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N/A

and surface area within the carbon by treating with a base facilitating pyrolysis. The carbon is then functionalized with metal oxides using a unique method. The metal oxides introduced to the carbon enhances the capture selectivity toward CO_2, which can be improved further in the presence of moisture. The sorbent design can easily be scaled up to kilogram levels at low cost due to its simple preparation method, which doesn't involve any expensive catalysts or template use. The high surface area property of carbon brings the advantage of well-distributed metal oxides throughout the sorbent. High CO_2 uptake capacity (4–7 wt%), at even 400 ppm, can be achieved with this design. While abundancy and low cost of coal are expected to further lower the total sorbent cost, the unique functionalization strategy can tailor the CO_2 interaction potential of the sorbent. This sorbent design has the ability to tune the porosity and the level of metal oxide functionalization. Therefore, optimum sorbent regenerability can be achieved and the heat requirement for the regeneration of the sorbent can be minimized. The team is collaborating with a computational team at NETL to optimize CO_2 sorption properties of the sorbent. Computed properties of the carbon, such as pore structure and the nature of the CO_2 interaction with the functional groups, are used to guide experiments to optimize the sorbent for the DAC process. It is also noteworthy that sorbent stability is very important for sustainable DAC. The proposed sorbent will exhibit high stability and mitigate major stability problems (i.e., pores collapsing over time and amine leaching) associated with MOFs and silica-based sorbents, respectively. The sorbent may also be fabricated to hydrophobic materials to be used in high-humidity air.

technology advantages

- Sorbent design can easily be scaled up to kilogram levels at low cost due to its simple preparation method.
- High surface area of carbon facilitates distribution of metal oxides throughout the sorbent.
- Abundancy and low cost of coal are expected to lower the total sorbent cost.
- Ability to tune the porosity and the level of metal oxide functionalization to optimize sorbent regenerability and minimize regeneration heat requirement.
- Sorbent exhibits high stability.

R&D challenges

- Creating high surface area and porosity (micro/mesoporous) in carbon.
- Effective functionalization of the sorbent with metal oxide groups.
- Ability to adjust porosity and the level of functional groups in carbon.
- Successful computational study to optimize the sorbent properties.
- Achieving high CO_2 uptake capacity between 4–7 wt% CO_2 at 400 ppm.
- Cost-effective CO_2 regeneration.

status

Porous carbon sorbents from coal with high porosity (micro/mesoporous) were synthesized and functionalized with metal oxide, which was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. Functionalization and testing are ongoing to optimize the sorbent performance.

available reports/technical papers/presentations

N/A.

Systems Analysis and Programmatic Support, Pathway Evaluation, and Benefits Analysis and Tool Development

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new methods to provide foundational analytical support that ties accomplishments in the laboratory to results in real-world systems. One objective is to identify the most promising carbon capture technology pathways and attributes in terms of cost, performance, and environmental impact. For example, post-combustion carbon capture research and development (R&D) has been generally focused on three technology pathways (membranes, solvents, and sorbents), which provide options to reduce the energy and cost penalties associated with carbon capture. This research focuses on accelerating the development of efficient cost-effective technologies that meet the programmatic goals for carbon capture: to develop transformational technologies that are ready for demonstration by 2030 and that can achieve 95% carbon dioxide (CO_2) purity with a cost of less than $30/tonne of CO_2 captured. Development efforts are consistent with the overall goal of reducing the time required to develop new carbon capture technologies.

technical goals

- Development and assessment of goals and metrics for the U.S. Department of Energy's (DOE) Carbon Capture Program.
- Setting protocols and standards for evaluating the cost, performance, and environmental impact of technology within the program.
- Conduct process, cost, and life cycle analysis (LCA) for multiple carbon capture pathways and specific extramural projects.
- Develop tools for dissemination to researchers and technology developers to aid in techno-economic analysis (TEA).
- Identify the most promising opportunities for deployment of transformational carbon capture technology and the implication of market, regulatory, and policy drivers on R&D decisions.

technical content

Systems analysis is a major emphasis in the Carbon Capture Program's portfolio and covers a variety of topics. These include TEA screening of new carbon capture technologies, systems design, goals and metrics development, and market analyses. These activities provide predictions on the cost and technical viability of carbon capture technologies for both intramural NETL-RIC projects, as well as extramural projects, and provide an unbiased analysis to inform the Carbon Capture Program.

Task 2—Systems Analysis and Programmatic Support

project focus:

Carbon Capture Systems Analysis

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402 (Tasks 2, 3, 4)

predecessor project:

2020 Carbon Capture FWP

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This task objective is to provide the foundational analytical support for establishing targets to evaluate the effectiveness of the Carbon Capture Program and its broadening portfolio. This includes the development and assessment of goals and metrics for the program, with emphasis on industrial capture, direct air capture (DAC), and biomass energy with carbon capture and storage (BECCS); setting protocols and standards for evaluating the cost, performance, and environmental impact of technology within the program; and meeting general programmatic and analysis support needs. Government accountability efforts require the establishment of appropriate goals for programs, as well as the periodic assessment of progress made against these goals. Evaluations of progress provide information needed by program and research management regarding future R&D directions. Enabling researchers and developers to conduct their analysis on a common basis in as standard of a methodology as possible allows for more technology information to be brought forward with the possibility of meeting the program goals.

Of particular emphasis in execution year 2021 (EY21) is the examination of areas new to the Carbon Capture Program in terms of goals, including, but not limited to, industrial capture, DAC, and the use of biomass for net-neutral or net-negative carbon systems. These areas have not been adequately evaluated in past goal analysis efforts and provide individual challenges for determining program goals. Efforts will be built upon prior extensive work in determining goals for post-combustion capture for pulverized coal-based plants, along with the EY20 examination of natural gas combined cycles (NGCCs). Reevaluation of cost of electricity (COE) and breakeven sales price reduction potential will support efforts to revise Office of Fossil Energy and Carbon Management (FECM) and Carbon Capture Program goals. Alternative terms for measuring technology advancement will also be examined to see if parameters that incorporate the wide variety of feed CO_2 concentrations and higher overall rates of CO_2 capture can be encompassed.

Task 3—Capture Technology Pathway Evaluation

This task aims to identify the most promising carbon capture technology pathways and attributes in terms of cost, performance, and environmental impact for a variety of feed CO_2 concentrations and capture rates. This is to be achieved through conducting process, cost, and LCAs for multiple carbon capture pathways and specific extramural projects, and by developing tools for dissemination to researchers and technology developers to aid in TEAs.

Information that ties accomplishments in the laboratory to results in real-world systems enables R&D to progress at lower costs and with greater stakeholder confidence. This type of information is also required to perform a TEA and LCA to evaluate if performance data (from laboratory to pilot-scale testing) provides progress toward program goals or sets targets for the performance data based upon the results of a TEA and LCA. Evaluations will inform multiple aspects of the DOE/NETL Carbon Capture Program, including aiding decision-makers in determining R&D progress toward meeting relevant DOE/NETL goals, assisting establishment of project/technology-specific performance targets, and informing project management about specific technology progress and R&D directions that best align with progress toward DOE goals.

Task 4—Carbon Capture Deployment Analysis (Benefits Analysis and Tool Development)

The task objective is to identify the most promising opportunities for deployment of transformational carbon capture technology and the implication of market, regulatory, and policy drivers on R&D decisions. This will occur through examination of those drivers, deployment potential, benefits of successful carbon capture technology development, and impacts on the overall system impact of deep decarbonization technologies. This includes enhancement of the representation of carbon capture technologies in domestic and international energy-economy models that are used by a wide variety of stakeholders to inform critical topics concerning energy policy. Model development and analyses will examine various business models for carbon capture demonstration and deployment with an emphasis on retrofitting existing sources of CO_2.

Development of enhanced capabilities in the area of carbon capture and storage (CCS) representation for energy-economy models and performing analysis with these capabilities helps to ensure that the importance of NETL R&D can be communicated in terms of economic and environmental impacts. Application of these models under a variety of scenarios, and including the inputs of successful R&D for CCS technologies, provides credible estimates for the value of R&D performed by NETL. Careful, systematic evaluation of carbon capture retrofit business models is required due to the breadth of technology and business options available. Opportunities for financial benefits may be realized from a variety of factors, both internal and external to the power plant boundary. A study describing business models in detail and evaluating them on a common and consistent basis will provide valuable information for project developers and the program.

technology advantages

- Enables promising concepts to be more quickly identified through rapid computational screening of processes and devices.
- Reduces the time to design and troubleshoot new devices by using detailed, device-scale models to better understand and improve the internal behavior of complex equipment.
- Streamlines process design by using state-of-the-art optimization techniques that focus development on the best overall operating conditions and process configurations.
- Provides quantitative predictions of device and process performance during scale-up based on rigorously validated simulations that consider model and parameter uncertainty.

R&D challenges

- Application of expert engineering judgment to the synthesis of systems to establish cost and performance entitlement.
- Inconsistency has been noted when comparing results of sensitivity studies and optimization.
- Only two of the six decision variables (absorber and stripper packing height) are manipulated in the optimization, whereas the sensitivity analysis demonstrates significant reduction in the objective function as the flowrate of antisolvent is increased. A significant amount of rigorous troubleshooting will be needed to remedy this situation.
- Ongoing adjustment and revision of the Carbon Capture Simulation Initiative (CCSI) Toolset software is required to meet the specific needs of each project, which often include rigorous first-principles modeling approaches not previously explored.

status

Systems Analysis and Programmatic Support

This task supported DOE/NETL with systems analysis at programmatic and larger R&D community levels. Specific studies were focused on advanced ultra-supercritical (AUSC) pulverized coal plants with CCS for the evaluation of coal plant goals with CCS consistent with Revision 4 of the Bituminous Baseline. After these results were determined, the focus shifted to NGCC, industrial, and negative emissions sources.

A quick turnaround effort was performed in January 2021 to determine the possible cost reductions and performance improvements for NGCC systems with advanced CO_2 capture to aid in developing targets for an upcoming NETL Funding Opportunity Announcement (FOA).

A nearly two-year international effort culminated in a series of papers and presentations at the 15th International Energy Agency Greenhouse Gas Technologies Conference (IEAGHGT) on the cost guideline work, titled “Towards Improved Guidelines for Cost Evaluation of Carbon Capture and Storage.” An overall white paper was published open access on March 30, 2021, and then reposted on NETL’s website on May 4, 2021. The report covered three main areas:

- Improved cost guidelines for advanced low-carbon technologies.
- Improved cost evaluation of CCS from industry.
- Improved guidelines for uncertainty analysis of CCS techno-economic studies.

Capture Technology Pathway Evaluation

A draft report was created for carbon capture in NGCC with exhaust gas recycle (EGR). This technology aims to increase the flue gas CO_2 concentration to aid in carbon capture (lower energy use and capital cost for absorber) by using recycled flue gas in the turbine instead of some of the typical excess air. The study results show that for solvent-based CO_2 capture, minimal gains are achieved through the use of EGR. Additional analysis is needed to determine if the effects of EGR are more prominent for membranes, sorbents, or systems that use a physical separation mechanism.

Final comments were addressed on an updated report for biomass with CCS. This report combines a TEA of post-combustion capture on a pulverized coal power plant with hybrid poplar co-feed up to 49% biomass with an LCA of the same TEA cases and an additional case of 100% biomass.

Final updates based upon recent calculations were made to the solvent and sorbent DAC case study reports prior to internal review and quality assurance/quality control review. Updated calculations provide additional perspective on the required performance of monolithic contactors to approach the cost of capture reported in the literature for some sorbent technologies and to approach similar cost of capture as estimated for solvent technologies. Both reports are under peer review prior to publication.

Carbon Capture Deployment Analysis (Benefits Analysis and Tool Development)

During EY20, the project for development of market incentives for CCS was kicked off and several meetings were held to define the scope and deliverables. The National Regulatory Research Institute (part of the National Association of Regulatory Utility Commissioners) will be preparing the report on proposed market initiatives to further incentivize the deployment of CCS.

During EY20, the team participated in the Energy Modeling Forum (EMF) 34 project using the Market Allocation (MARKAL) model. In addition to the core scenarios run for the EMF 34, the team also ran several CCS-specific scenarios, including the first characterization of DAC technologies in the model. The team plans to continue participation in the EMF and to share technology assumptions and inputs regarding CCS technologies, including DAC and hydrogen pathways.

available reports/technical papers

NETL Energy Analysis Website: *https://netl.doe.gov/ea/about*.

Roussanaly, S., Rubin, E. S., van der Spek, M., Booras, G., Berghout, N., Fout, T., Garcia, M., Gardarsdottir, S., Kuncheekanna, V. N., Matuszewski, M., McCoy, S., Morgan, J., Nazir, S. M., & Ramirez, A., “Towards Improved Guidelines for Cost Evaluation of Carbon Capture and Storage,“ White Paper on Point Source Carbon Capture April 2021. *https://netl.doe.gov/projects/VueConnection/download.aspx?id=f5bb7f59-9f44-4503-bc5c-818d82b58e5d&filename=TowardsImprovedGuidelinesforCostEvaluationofCarbonCaptureandStorage_042921.pdf*.

Carbon Capture Simulation for Industry Impact (CCSI²)

primary project goal

The primary goal of the Carbon Capture Simulation for Industry Impact (CCSI²) project is to utilize the computational tools and models developed under the Carbon Capture Simulation Initiative (CCSI) in partnership with industry to accelerate and de-risk the scale-up of new and innovative carbon capture technology. The CCSI² operates in conjunction with and in support of the U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) to focus on advancing promising technologies.

In 2010, DOE initiated CCSI to help reduce the amount of time that it historically takes to develop and scale-up new technologies in the energy sector, which traditionally takes up to 15 years to move from the laboratory to pre-deployment, and another 20 to 30 years for mature, industrial-scale deployment. Advanced modeling and simulation is developed and applied to enable more rapid and lower-cost capture technology development at reduced risk during the commercialization process.

technical goals

The team assists the Carbon Capture Program and technology developers by providing:

- Detailed understanding of capture materials through system performance under parametric uncertainty.
- Designs for high performance and intensified unit operations.
- Synthesis of processes optimized for novel materials.
- More informed design, operating, and control decisions.
- Modeling, optimization, and test campaign support for small and large pilots.
- Optimized processes under uncertainty.
- Intelligent design of experiments (DoE) at all Technology Readiness Levels (TRLs) for model refinement, system optimization, and acceleration of deployment.
- Machine learning (ML) frameworks to reduce computational time.
- Support for the Framework for Optimization and Quantification of Uncertainty and Surrogates (FOQUS), which will centralize and integrate computational capabilities critical to the Carbon Capture Program and CCSI² mission.

technical content

In support of the Carbon Capture Program, CCSI² maintains the CCSI Toolset, released to the public as open-source software, and continues to prepare tools, document capabilities and instructions for use, manage a public repository, and implement a release management system for subsequent versions of the tools.

CCSI² is led by the National Energy Technology Laboratory (NETL) and leverages the DOE national laboratories' core strengths in modeling and simulation. In full pursuit of the CCSI² vision, this project integrates the modeling and simulation capabilities at NETL and complements them with essential, world-class expertise

project focus:

Advancing Carbon Capture Technology Scale-Up

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022422

predecessor project:

2020 CCSI² FWP

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partners:

Los Alamos National Laboratory; Lawrence Berkeley National Laboratory; Pacific Northwest National Laboratory; Lawrence Livermore National Laboratory; Oak Ridge National Laboratory; West Virginia University; University of Texas-Austin; University of Toledo; University of Notre Dame; University of Pittsburgh; Carnegie Mellon University at Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), Pacific Northwest National Laboratory (PNNL), and Oak Ridge National Laboratory (ORNL) in its core national laboratory consortium.

Carbon capture is critical to significantly reducing domestic and global carbon dioxide (CO_2) emissions. However, the energy and capital cost associated with carbon capture systems is prohibitive for deployment. Today's cost to capture CO_2 using state-of-the-art carbon capture technologies must be reduced to competitive levels more rapidly and at lower risk. FECM goals are for technologies under development to be ready for commercial deployment by 2030 and must be on a pathway to capture at least 95% of generated CO_2 and achieve 20% reduction in captured cost for natural gas combined cycle (NGCC) power plants relative to the baseline case without carbon capture and storage (CCS; excluding transportation and storage costs). Prior requirements for 90% CO_2 capture have been increased, which introduces the challenge of increasing CO_2 capture while mitigating cost increases. Balancing cost management with a high level of CO_2 capture meaningful enough to contribute to climate change mitigation is critical in this new approach, yet the balance introduces a great deal of additional complexity. CCSI^2, with proven cost-performance optimization frameworks, is ideally positioned to apply the CCSI Toolset to provide well-informed perspective on the most impactful areas of research to achieve these more aggressive decarbonization goals.

The CCSI^2 team provides fundamental analysis, modeling, and optimization of carbon capture technology by working closely with industry partners. The CCSI^2 team efficiently identifies data collection needs, computationally and experimentally characterizes carbon capture materials, designs and optimizes prototype devices and processes, and fully propagates uncertainty in model predictions for a complete perspective on results accuracy.

For Execution Year 2022 (EY22), the work is organized under several tasks, including NGCC Pilot Support, General Capture R&D Program Support, CCSI Toolset Community Support, and Support for Industrial Capture Applications. The task for General Capture Program support focuses on increasing the impact of research and development (R&D) by generating and applying computational frameworks to support carbon capture technology research. The subtasks include Computational and Experimental Support for CO_2 Absorber Process Intensification, Monoethanolamine (MEA) Modeling and Cost Analysis of High Capture Rates, and Robust Optimization of Solvent-based System Designs.

The CCSI Toolset Community Support task manages the open-source CCSI Toolset and facilitates active development, deployment, and maintenance of the CCSI Toolset software, with updated features, capabilities, and documentation, by and in support of the research efforts within other subtasks of CCSI^2. This subtask includes the development of Sequential Design of Experiments (SDoE) to optimize experimental data generation, and development of Machine Learning approaches to increase the efficiency of the computational fluid dynamics models that support process intensification. This subtask also includes the education of contributing developers from these subtasks on mature software development practices and tools, as well as active support and outreach to new users and stakeholders.

The Pilot Support task supports Carbon Capture Program projects scheduled for pilot testing of carbon capture technologies at Technology Centre Mongstad (TCM). Support includes the development of materials, device, and process models with sufficient uncertainty quantification to support the DoE required to maximize knowledge gained from the TCM test campaigns. The aim is to leverage and improve modeling during each campaign to reduce the time and cost while maximizing productivity of each campaign. Four technology developers will be piloting solvent-, membrane-, and sorbent-based capture technologies and all will require DoE support. Each technology developer is also interested in optimizing their system's operation and potential configuration to reduce thermodynamic penalties, reduce cost, and minimize environmental impact (e.g., solvent emissions).

The CCSI^2 EY22 tasks have seven thrusts:

1. Provide direct support to the small natural gas pilot projects recently awarded by the Carbon Capture Program. This work ensures advanced materials development efforts are integrated with advanced systems design, analysis, and optimization, as well as supports SDoE to maximize the value of the test campaign. Additionally, the desired outcome is to enhance computational capabilities for generalized natural gas solvent and sorbent frameworks for multi-scale, integrated materials, device, and process optimization.
2. Develop a formalized SDoE methodology that will strive for data generation at all TRLs that is optimized for a variety of objectives (i.e., model refinement, process optimization, etc.). The desired outcomes are to continue adding relevant capability for computational SDoE for steady state and dynamic processes into FOQUS. This includes non-uniform space filling and input response space filling experimental designs, which more effectively leverage and inform equation-based modeling efforts than more conventional uniform space filling approaches. SDoE focuses on maximizing learning while reducing the time and cost of generating useful experimental results. SDoE can also be used to increase the efficiency of computationally intense, simulation-based experimentation; develop constrained

experimental designs to consider operational and/or safety restrictions; and develop experimental designs to focus on exploration of model output directly relevant to programmatic goals.

3. Inform R&D efforts in projects supported by the Carbon Capture Program through fundamental modeling, analysis, and optimization. The desired outcomes are the continued development of a modeling framework that supports superstructure-based advanced flash stripper process synthesis framework for generic solvents, accurate wetted area calculational framework for estimating generic packing and generic solvents to inform device performance, and transfer lessons learned from coal-based modeling to natural gas-based applications.
4. Support the open-source release of the CCSI Toolset. The desired outcome is to upgrade the open-source Toolset release to communicate with more modeling platforms required for the direct support of the Carbon Capture Program, including interfacing with a new ML tool under development that will automate the development of surrogate computational fluid dynamics (CFD) models.
5. Continue to support the Carbon Capture Program projects funded to pilot their CCS technology at TCM. The desired outcomes are to complete modeling of Research Triangle Institute's (RTI) non-aqueous solvent (NAS) system performance and aerosol emissions, which will support the SDoE for the TCM pilot tests, and continue Membrane Technology and Research Inc. (MTR) membrane modeling and TDA Research Inc. (TDA) sorbent modeling, which will support their own SDoE.
6. Continue device-scale intensification and optimization. The desired outcomes are to continue computationally developing intensified device designs that will consolidate process operations, reducing equipment requirements and improving performance. CCSI^2 will provide computational designs that can be realized with cutting-edge 3D-printing technology and that will provide performance improvement beyond that of conventional equipment; develop equipment models that fully characterize solvent-packing interactions including hydrodynamics, heat/mass transfer, and solvent chemistry; reduce the computational complexity by integrating with ML approaches to increase the speed of convergence while sustaining high predictive accuracy; and work with the 3D-printing community to use intensified CO_2 capture absorber modeling to inform advanced manufacturing processes.
7. Support industrial CCS. The desired outcome is to provide an understanding of how CCS could be integrated into a cement plant such that tradeoffs between the techno-economic performance of the CO_2 capture system and its effects on the base cement plant and product quality are optimally balanced.

technology advantages

The CCSI^2 team engages carbon capture technology developers for direct and widespread support of priority interests of the Carbon Capture Program with the aim to fully understand and exploit the unique behavior of recently developed transformational carbon capture materials and equipment. CCSI^2 continues developing a technical understanding of CO2 system operation in ways that will serve to guide R&D required for an electrical grid evolving to incorporate more intermittent renewables. CCSI^2 is constantly developing a more comprehensive understanding of CO_2 capture technology for applications including natural gas and industrial sources, at increasing and deeper levels of decarbonization. CCSI^2 is also positioned to address issues related to direct air capture of CO_2 to effectively address the more difficult to decarbonize sectors like transportation.

The open-source CCSI Toolset (1) enables promising concepts to be more quickly identified through rapid computational screening of materials, equipment, and processes; (2) reduces the time to understand, design, and improve new, intensified devices by developing detailed device-scale models; (3) fundamentally characterizes steady state process operation and dynamic process operation for extended understanding of process flexibility and control; (4) optimizes process design with a suite of state-of-the-art algorithms that target the best overall operating conditions and process configurations; (5) provides a comprehensive computational framework for systematic experimental design optimal to the objectives defined by the testing protocol; and (6) provides quantitative predictions of material, device, and process performance during scale-up based on rigorously validated simulations that take into account model and parameter uncertainty.

R&D challenges

- Identification and rigorous quantification of scale-up uncertainty and model enhancement to reduce such uncertainties.
- Technology-specific challenges in development of various transformational carbon capture materials and equipment.

status

CCSI^2 released the FOQUS version 3.13.1; support for the software continues to fix bugs and add capabilities directly supporting the analysis needs of the Carbon Capture Program. CCSI^2 is continuing collaboration with three technology developers to support pilot tests of their carbon capture technologies at TCM over the next three years. Collaboration with RTI continues under the Non-Disclosure Agreement (NDA) with NETL, which permits sharing of models and data. CCSI^2 has initiated Cooperative Research and Development Agreements (CRADAs) with RTI and MTR, which will permit data/model exchange amongst all participating CCSI^2 laboratories to begin collaboration. TDA has collaborated with CCSI^2 by sharing sorbent contactor performance data to support model development for the SDoE of the TCM pilot.

available reports/technical papers/presentations

CCSI^2 Website: *https://www.acceleratecarboncapture.org*.

CCSI Toolset: *https://github.com/CCSI-Toolset/*.

CCSI^2 Publications List: *https://www.acceleratecarboncapture.org/publications*.

“Overview of Carbon Capture Simulation for Industry Impact (CCSI^2) Project,” presented by Michael Matuszewski, 2021 Carbon Management and Oil and Gas Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Matuszweski.pdf*.

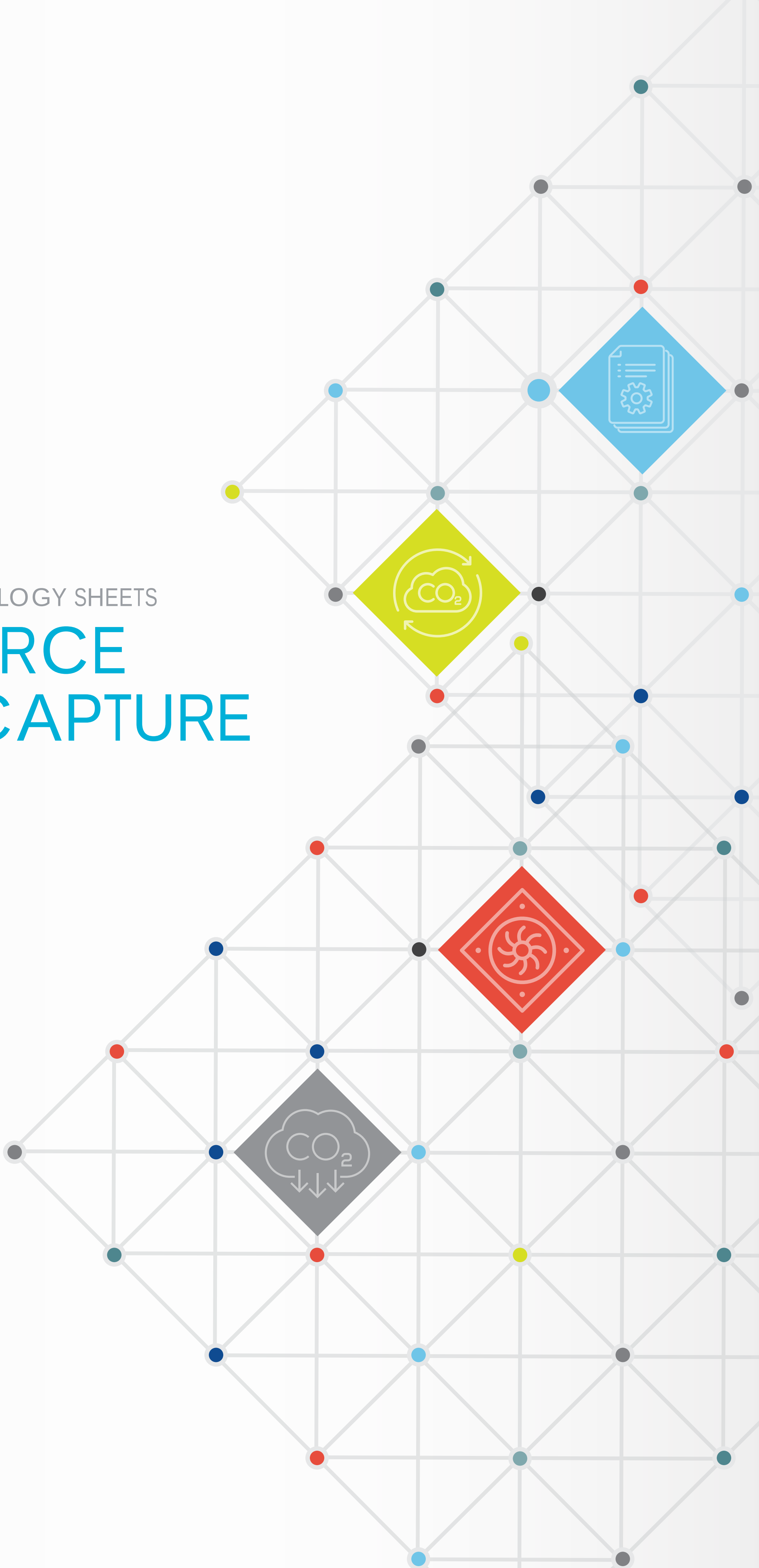
“CCSI^2 Brief: Computational Support for the Carbon Capture Program,” presented by Benjamin Omell, DOE-NETL’s 2020 Integrated Project Review Meeting, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Omell.pdf*.

“CCSI^2 Project Overview,” presented by Michael Matuszewski, 2018 NETL CO_2 Capture Technology Project Review Meeting, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/M-Matuszewski-CCSI2-Capture-Impact-Simulation.pdf*.

“CCSI^2 and Toolset Support Program Overview and Toolset Introduction,” presented by Michael Matuszewski, 2017 NETL CO_2 Capture Technology Project Review Meeting, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/3-Wednesday/M-Matuszewski-CCSI2-Program-Overview.pdf*.

CARBON CAPTURE TECHNOLOGY SHEETS

POINT SOURCE CARBON CAPTURE



UK-CAER Heat-Integrated Transformative CO_2 Capture Process for Pulverized Coal Power Plants

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER) team developed a transformational post-combustion carbon dioxide (CO_2) capture technology using advanced solvents and incorporating innovative heat integration methods to utilize heat typically rejected to the environment via a two-stage solvent regeneration configuration and several novel process intensification strategies, thereby ultimately improving power plant efficiency.

UK CAER prepared a front-end engineering design (FEED) study for a 10-megawatt-electric (MWe) large pilot plant based on the technology demonstrated at the 0.7-MWe scale.

UK CAER advanced its four-pronged CO_2 capture approach that includes process intensification, two-stage stripping, heat integration, and an advanced solvent by completing the design of a 10-MWe capture system for a coal-fired power plant. Phase I has been completed and consisted of: (1) selection of a host site for Phases II and III; (2) creation of Aspen Plus® model simulation; (3) completion of an environmental information volume (EIV); and (4) determination of Phase II team and cost-share commitments. Phase II efforts consisted of a detailed FEED study, National Environmental Policy Act (NEPA) permitting and documentation, and Phase III cost-share commitments.

technical goals

Phase I objectives were to:

- Reinforce the formation of a cohesive project team covering technology development; solvent development; environmental, health, and safety (EH&S); engineering design, fabrication, and construction management; technology commercialization; and end-user utilities.
- Select and secure a host site and carbon capture system location.
- Update heat and material balances with the most recent small-scale experimental data and chemical composition to complete and improve accuracy of an EIV and process design package for the proposed UK CAER CO_2 capture technology, including the cost and schedule.
- Secure commitments from an engineering design firm, NEPA contractor, technology partners, and vendors.
- Update preliminary costs and schedules for Phases II and III.
- Secure commitments for Phases II and III cost share.

Phase II objectives were to:

- Complete a FEED study for the proposed large-scale pilot, including a detailed cost and schedule estimate for Phase III for the installation of the 10-MWe pilot at the host site, followed by commissioning, start-up, testing, operations, and data collection for performance validation.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Advanced Solvents, Heat Integration, and Process Intensification

participant:
UK Research Foundation

project number:
FE0031583

predecessor projects:
FE0026497; FE0012926; FE0007395

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partners:
Carbon Clean Solutions USA; Smith Management Group; Carbon Management Research Group; Electric Power Research Institute; Huaneng Clean Energy Research Institute; Koch Modular Process Systems; Worley; Membrane Technology Research; University of Texas at Austin; Trimeric Corporation; Louisville Gas and Electric and Kentucky Utilities; Integrated Test Center; Carnegie Mellon University

start date:
04.01.2018

percent complete:
100%

- Complete the NEPA process at the host site.
- Submit permitting documentation to appropriate authorities and obtain the air permits for the steam generator and carbon capture system units.
- Document secured cost share for Phase III.
- Secure commitments for all necessary Phase III team members, including an engineering, procurement, and construction (EPC) vendor or equivalent to complete construction.
- Update the techno-economic analysis (TEA) for the UK CAER technology integrated with a 550-MWe net supercritical pulverized coal power plant based on the most recent system design and cost information.

technical content

UK CAER's four-pronged approach to CO_2 capture that includes process intensification, two-stage solvent regeneration, heat integration, and an advanced solvent has evolved over a series of projects in recent years. Currently, the proposed capture process system incorporates several energy-saving and performance-enhancing features, among which the most notable are as follows:

- A two-stage solvent regeneration configuration, consisting of a steam-driven, first-stage primary stripper removing most of the CO_2, followed by a secondary stage designed as an air stripper powered by recovered heat from the carbon capture system block at the CO_2 compressor intercoolers, and the primary and secondary stripper overhead streams. The two-stage stripping reduces the carbon loading in the lean solvent to very low levels, and the exiting CO_2-laden air is fed into the boiler as combustion air to boost the CO_2 concentration at the absorber inlet. The system integration and heat recovery scheme has been demonstrated through small-pilot scale experimentation and simulation. The secondary stripper also provides direct cooling to the lean solution returning to the absorber, significantly reducing the duty of the indirect-cooled lean solvent polishing exchanger; therefore, the additional capital cost of the second stripping column is offset by heat exchanger and cooling tower savings. Another advantage of the two-stage solvent regeneration scheme is that ion-free water carried by saturated air from the up-stream water evaporator is added to the solvent loop in the secondary stripper, eliminating the complexity, equipment, chemicals, and power needed to produce de-ionized water for amine loop makeup.
- Applied process intensification technologies, including:
  - Three discrete packing sections in the absorber with in-situ gas-liquid distributors at every 5 to 10 feet of structured packing for high volumetric effectiveness and less gas-liquid channel flow.
  - Membrane CO_2 pre-concentration prior to the absorber inlet applied, as needed, to boost carbon loading in the rich solvent. Outputs from membrane consist of retentate enriched in CO_2 and permeate depleted in CO_2. These two flue gas streams are introduced at different levels in the absorber column, with the lean stream injected higher in the column where fresher solvent is present, and the rich stream injected farther down.
  - A split rich feed to the primary stripper to reduce the reboiler steam requirement and decrease the water content in the exit gas stream. The rich amine stream is split with a portion being heated to approximately 180°F (solvent- and stripping-dependent), and fed to the top of the stripper packing, acting as a heat sink to condense the water vapor and reduce the exit gas water (H_2O)/CO_2 ratio. The remaining rich flow is further heated to generate two-phase flow that is fed to the middle of the stripper packing, acting as a second source of carrier gas for CO_2 stripping. This may be accomplished with one lean/rich heat exchanger with two outlets, as shown in Figure 1, or with a series of two lean/rich heat exchangers.
  - Extracted steam exergy loss minimization through splitting of the feed water after the boiler feed water pump into two streams. While the main portion of the feed water maintains the normal flow path, 20 to 25% of the flow is heated to the same parameters as the boiler economizer in a split, last-stage feed water heater powered by steam extracted for the carbon capture system reboiler.
  - Solids incorporated in the absorber exit gas wash stream to minimize solvent entrainment and aerosols. By adding particles within the water wash stream, the solvent emission at the exhaust of the solvent recovery system is demonstrated to be less than the instrument detection limit.
- Has been demonstrated with various advanced solvents at the bench- and pilot-scales. Notably, the commercial Hitachi H3-1, Carbon Clean Solutions, USA (CCSUS) CDRMax and two UK solvent blends have been under investigation and have figured prominently in small-pilot testing. Corporate restructuring has resulted in H3-1 becoming commercially unavailable, but CCSUS is partnering with UK CAER at the large-pilot scale. To balance the cost of commercial solvents and the gain in performance benefits, the advisable approach to solvent development focuses on striking a good balance of moderate solvent cost with CO_2 absorption/desorption performance and

kinetics, including, but not limited to, cyclic capacity, solvent emissions, and degradation. This can be achieved by blending amines that are functionalized to prevent the formation of nitrosamines, using additives with catalytic kinetic function, or modifying solvent physical properties for additional gas-liquid interfacial areas and inhibitors to reduce solvent degradation and corrosion.

- Advanced process controls; UK CAER has developed two computing blocks, integrated with process control software such as Emerson DeltaV, to first determine the real-time, on-line alkalinity and carbon loading of the solvent using conventional instrumentation and then to manipulate the most effective control variables, such as lean solution circulation rate, lean loading, and liquid/gas temperature, in prompt response to external changes while ensuring minimum stream extraction is maintained.

Figure 1 depicts the general process arrangement of the UK CAER technology (most of these features are depicted here).

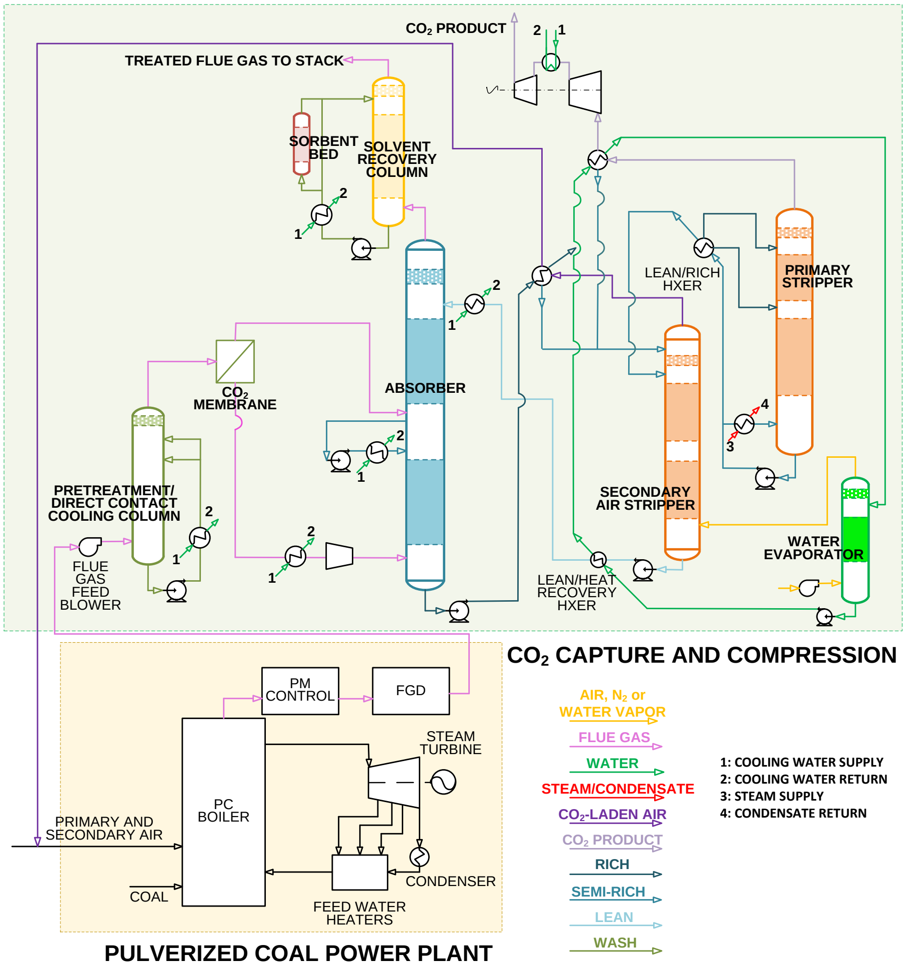

Figure 1: UK CAER carbon capture system process flow diagram.

Note: Black oval indicates the CO_2 pre-concentrating membrane unit investigated in FE0012926, which is not included in the large-pilot carbon capture system.

UK CAER's Advanced Solvents

UK CAER solvent development focuses on low-cost, enhanced CO_2 absorption kinetics; low emissions; and low degradation, considering both chemical and physical properties and the interactions between amine components of solvent blends and the additives. The overwhelming majority of research and development (R&D) in CO_2 capture solvents has focused on the amine chemistry, with little thought to the impact of additives on gas-liquid interface characterization. Understanding the impact of additives on key solvent properties – including surface tension and elasticity, wettability, and whether these impacts play a significant role in CO_2 capture characteristics such as absorption rate, degradation, and aerosol formation – are an important focus of R&D in this context.

UK CAER developed a novel catalytic amine solvent utilizing organometallic homogeneous catalyst chemistry to enhance CO_2 absorption kinetics. Mass transfer rate increases of 15 to 40% are possible by using a catalytic advanced amine solvent over an uncatalyzed amine solvent, resulting in more efficient absorption of CO_2, increased rich stream CO_2 concentration, and decreased absorber size requirements. Improved solvent thermal stability allows the solvent to be used in the high-temperature stripper conditions utilized in this process. Additional improvements from the catalytic solvent include increased cyclic capacity, reduced solvent loss and makeup requirements, and lower energy regeneration demand.

UK CAER designates solvents currently under investigation with codes to maintain confidentiality, reflecting permutations of proprietary commercial amine solvents. One of the solvents much investigated of late is CAER-B3, which is a hindered primary amine blend.

Discretized Packing in Absorber

For any advanced solvent, the absorber temperature bulge typically occurs 10 to 15% from the top of a uniformly packed section when operated under a low liquid/gas ratio. UK CAER bench experimental data has shown that with a discretized packing arrangement, the temperature profile is modified, moving the bulge down the column and resulting in a 5 to 11% increase in rich loading for the same heights of packing, depending on the solvent lean loading. With an ideal column temperature profile, significant CO_2 absorption rate improvements (2 to 4x) will result in a small absorber (25 to 50% size reduction).

Pressurized Primary Stripper with Split Rich Solvent Feeds

UK CAER developed a rich solvent split configuration using the traditional lean/rich heat exchanger with one additional warm rich solvent extraction port. During operation, up to 50% of the total rich flow is extracted at a temperature of approximately 180°F (solvent- and stripping-dependent) and fed to the top of the stripper packing. This acts as a heat sink to condense the water vapor and reduce the exit gas H_2O/CO_2 ratio. The remaining rich flow is further heated to produce a two-phase flow, with 2 to 6 wt% vapor concentration, enters the middle of stripper packing depending on stripper pressure and solvent properties. The produced vapor acts as a second source of carrier gas for CO_2 stripping. Combined with solvent regeneration under pressure, UK CAER modelling results indicate the H_2O/CO_2 ratio in the stripper exhaust is significantly reduced from conventionally 0.8 to 1.0, to 0.3 to 0.4 at 45 pounds per square inch (psi) stripper pressure, resulting in a steam consumption reduction of ~26%. This feature, in combination with CO_2 recycling, will result in a reboiler-specific energy of 950 British thermal units (Btu)/lb (2.2 gigajoules [GJ]/tonne) CO_2 captured for advanced solvents.

CO_2 Pre-Concentrating Membrane

Experimental results show that using a CO_2 pre-concentrating membrane to split the absorber gas feed into two streams (the permeate stream, with an enriched CO_2 concentration of 30 vol%, and the rejection stream, with a CO_2 concentration of ~10 vol%) yields a 30% energy savings compared to the conventional non-membrane configuration. Figure 2 shows the membrane separator for enriching CO_2 in the flue gas, and an actual polymeric membrane unit produced by Membrane Technology and Research (MTR), which was used in pilot-scale testing.

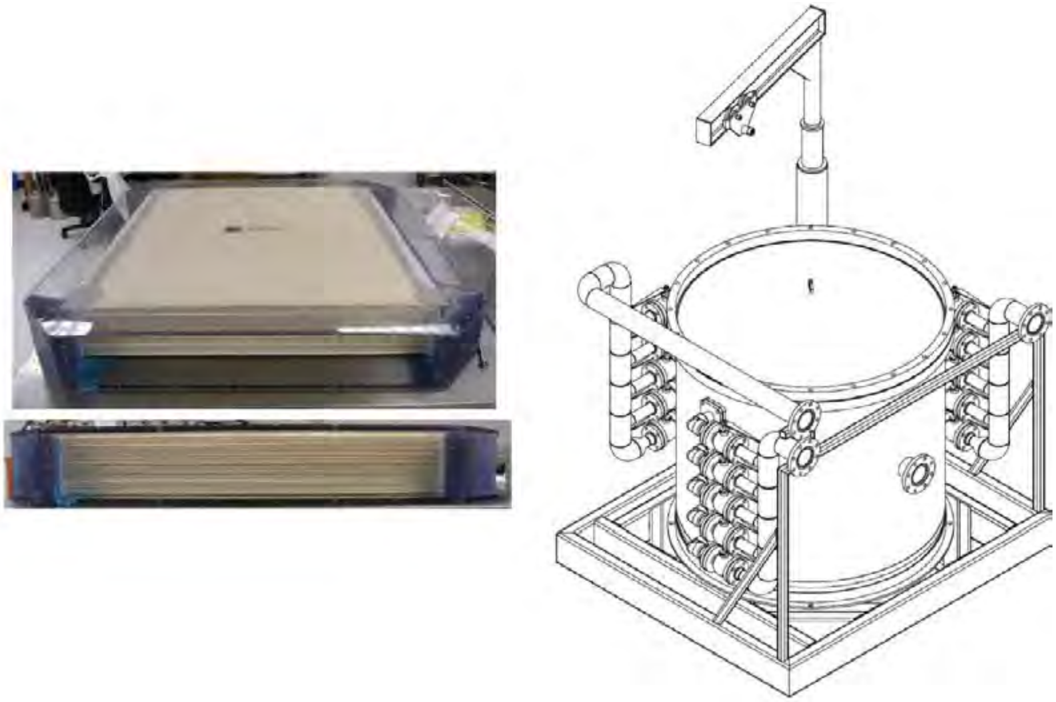

Figure 2: MTR CO_2 pre-concentrating membrane, internals on left and housing on right.

Membrane-Based Dewatering of Rich Amine Solvent

Related bench-scale project work (FE0012926) has extended the technology to include a membrane dewatering unit installed in the solvent rich stream. This feature is an integrated membrane concentrator unit intended to provide dewatering of the CO_2-rich amine solvent/solution exiting from the CO_2 absorber, either before or after the lean/rich heat exchanger. The membrane separator would selectively permeate water from the stream for recycle to the absorber through a zeolite-based membrane, as shown in Figure 3, effectively concentrating the CO_2-rich stream and increasing the CO_2 partial pressure, which can further reduce process energy demand. This membrane should be designed to maximize water permeability and carbon/amine rejection while maintaining stable performance over time. UK CAER has investigated zeolites as the material of choice for this membrane. Currently, given the membrane surface area required and the high cost of zeolite membranes, it is not practical to include it in process scenarios as envisioned. However, through the use of lower-cost hollow fiber support materials and increasing the packing density of the active membrane surface area up to >200 m^2/m^3, the economics of this enrichment process can be improved. In addition, through modifications to the active membrane layer and the permeability of the support layer, water flux through the membrane can be enhanced to further reduce the cost and implementation of this system in a CO_2 capture process.

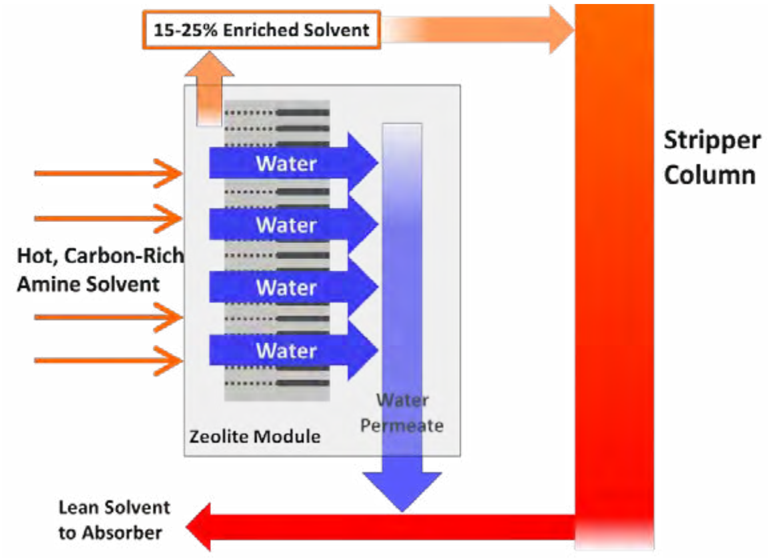

Figure 3: Solvent membrane dewatering for CO_2 enrichment.

Findings from Small Pilot Testing

Small pilot testing at 0.7 MWe has been performed at the Kentucky Utilities E.W. Brown Generating Station in Harrodsburg, Kentucky, using a process configuration including much of the scheme depicted in Figure 1. Performance of the capture system was baselined using a generic 30-wt% monoethanolamine (MEA) solvent to obtain data for direct comparison with the National Energy Technology Laboratory (NETL) Reference Case 10 (RC10). Also, Hitachi's proprietary solvent H3-1, CCSUS' proprietary solvent CDRMax, and the CAER blended solvents were tested. Parametric test campaigns, system transient dynamic studies, and long-term continuous verification tests of the heat integration process enabled characterization of the system response in terms of load-demand following, varying flue gas conditions, and individual component operation. Evaluation of solvent degradation, process emissions, and corrosion studies of materials in the circulating solvent were accomplished. See below, and also in the Other Parameters section following Table 2 for findings in these areas. Data were collected to support a full techno-economic and EH&S analysis for a 550-MW commercial-scale carbon capture plant.

Notable findings included:

- The process can easily capture 90% of CO_2 in flue gas using either MEA, H3-1, CDRMax, or CAER solvent as the working capture solvent.
- MEA solvent regeneration energy was determined to be 1,200 to 1,750 Btu/lb CO_2 captured, ~13% lower than RC10.
- H3-1 solvent regeneration energy was determined to be 900 to 1,600 Btu/lb CO_2 captured,~36% lower than RC10. Overall, low-regeneration energies are possible over a range of solvent concentrations.
- CDRMax solvent and the UK CAER solvent regeneration energies were determined to have similar performance, in the range of 1,150 to 1,400 Btu/lb CO_2 captured,~8 to 25% lower than RC10.
- The secondary air stripper is capable of regenerating >10% of the CO_2 captured, as depicted in Figure 4. At the commercial scale, the exhaust CO_2-laden air (8 to 12 vol% CO_2, dry) will be recycled back to the boiler as secondary combustion air, yielding a higher absorber inlet CO_2 concentration (15 to 17 vol%), which has been observed to always correspond to a low-solvent regeneration energy, and a relatively higher boiler efficiency.

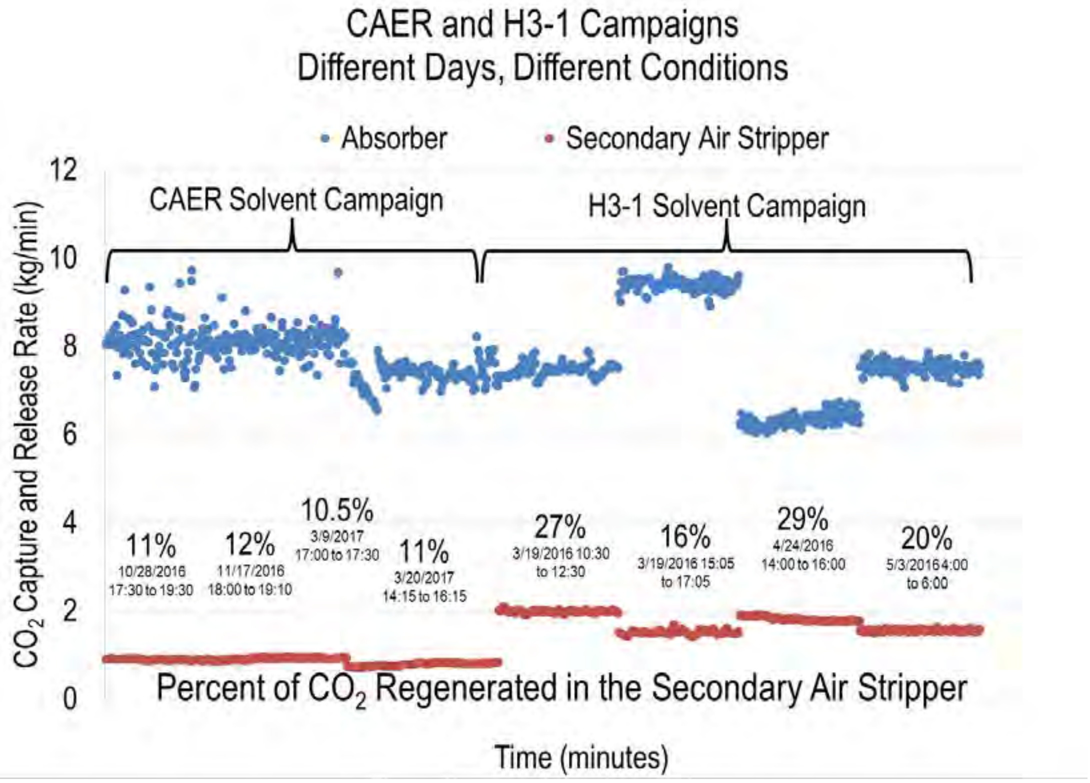

Figure 4: UK CAER secondary air stripper CO_2 regeneration.

- Varying ambient conditions have an impact on CO_2 capture, attributable to cooling water temperature variations that impact the capture system process stream temperatures at any point where heat exchange with cooling water is involved, including flue gas temperature, lean solvent return, and absorber interstage cooling resulting in variation of rich carbon loading and temperature at the absorber bottom.

- Adequate absorber liquid/gas distribution is required to maintain high absorber efficiency.
- Lean/rich exchanger performance is critical to the energy efficiency of the cycle: if the approach temperature in the exchanger is not kept low, the efficiency suffers. This is depicted in Figure 5, showing that an increase in approach temperature to 35°F from 20°F increases the solvent regeneration energy demand by about 400 Btu/lb CO_2.

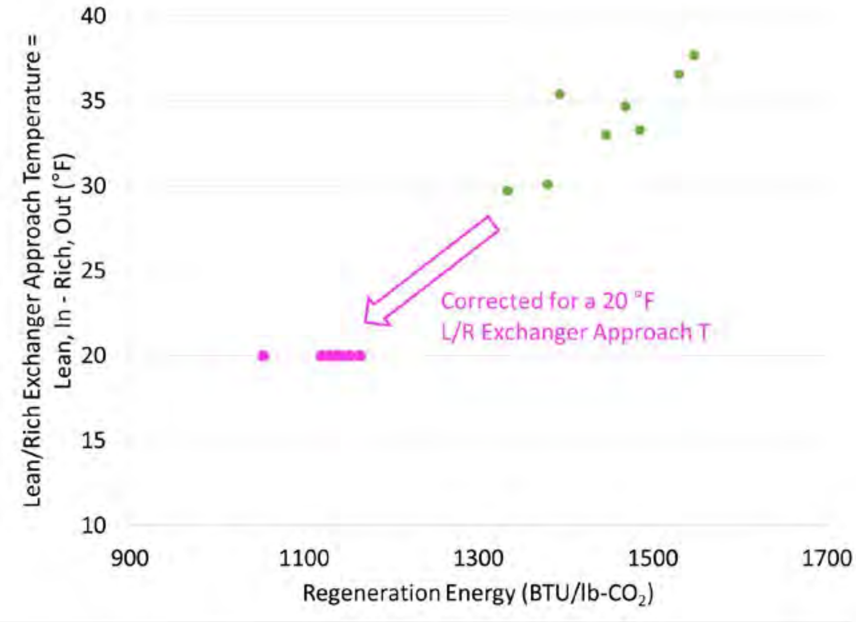

Figure 5: Effect of lean/rich heat exchanger approach temperature on solvent regeneration energy demand.

- The measured accumulation of chloride from the service water and heat-stable salt (HSS) contaminants from coal flue gas is depicted in Figure 6. While elemental accumulation in the solvent still needs to be monitored, because the UK CAER CO_2 capture system adds water to the amine loop directly via secondary air stripping loop with plant service water, this shows that the majority of accumulating contaminants originate in the coal flue gas, not the service water source, even without installation of demineralization devices such as reverse osmosis and ion exchange resin. Because accumulating species can cause various deleterious impacts, including solvent degradation and loss of absorption performance, corrosion of materials in the process circuit, etc., this is an area to continue investigating in future technology scale-up.

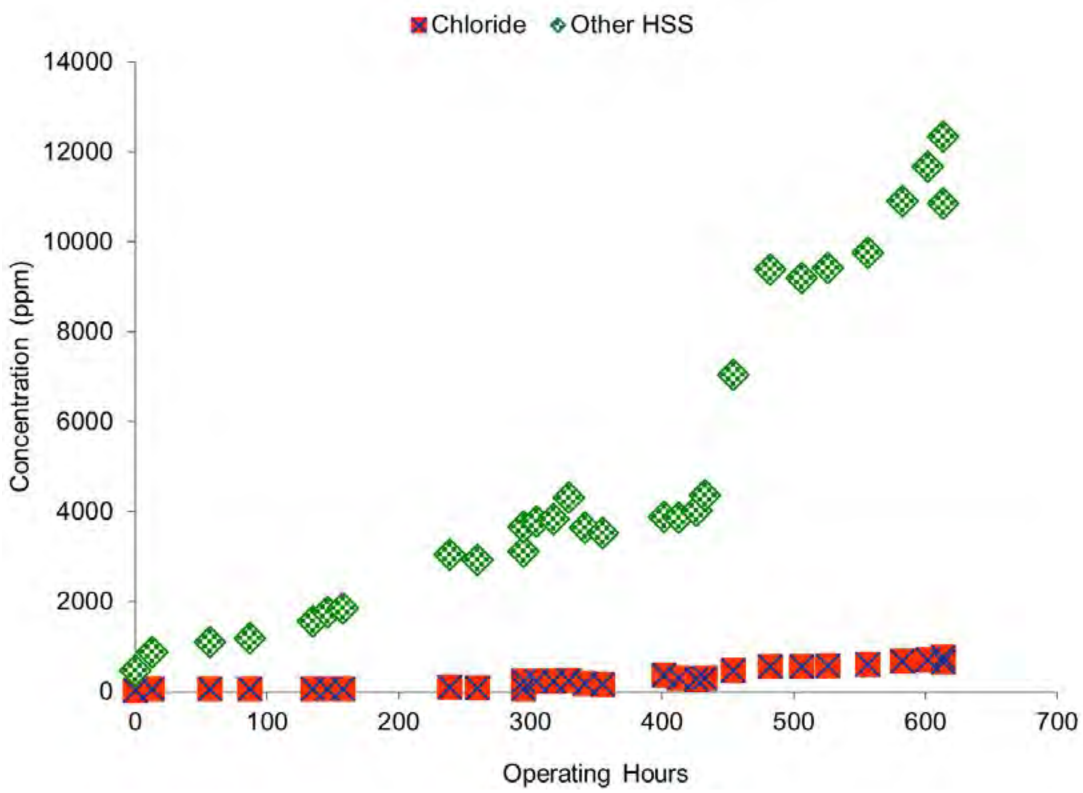

Figure 6: Accumulation of contaminants in solvent.

- Process emissions in the scrubbed CO_2-depleted flue gas from solvent degradation (as ammonia) were found to be related to increasing iron content in the solvent from corrosion, as depicted in Figure 7. Corrosion and solvent degradation can be controlled by adding a proprietary multi-functional additive to the solvent. Figure 8 shows that when the multi-functional additive concentration in the solvent is above the operating level of 100 parts per million (ppm), the ammonia emissions are low, but when the additive is depleted, solvent degradation and ammonia emissions increase.

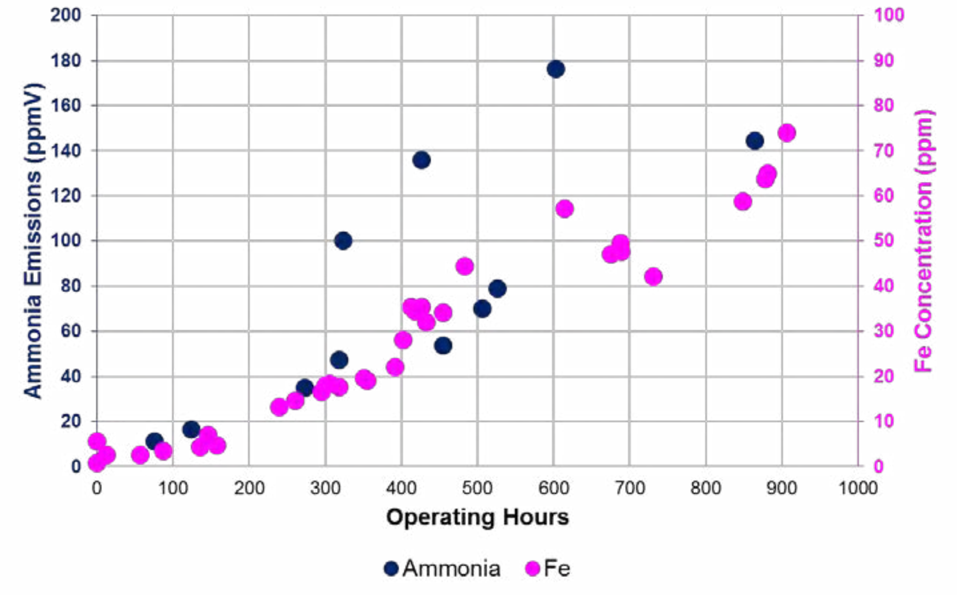

Figure 7: Ammonia emissions and iron.

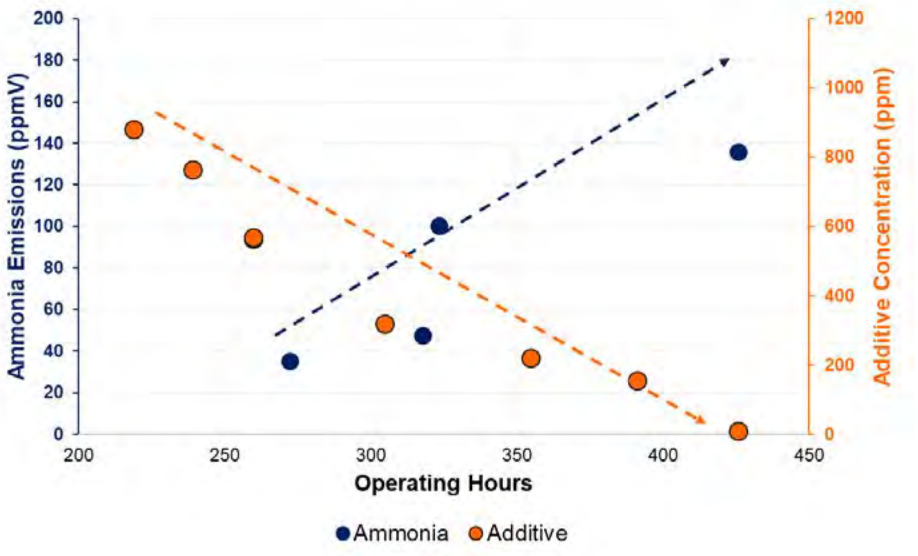

Figure 8: Ammonia emissions versus additive in the solvent.

Design of 10-MWe Pilot Plant

The design of the large pilot consists of 10 modules and includes a stand-alone absorber and a conventional cooling tower, as shown in Figure 9.

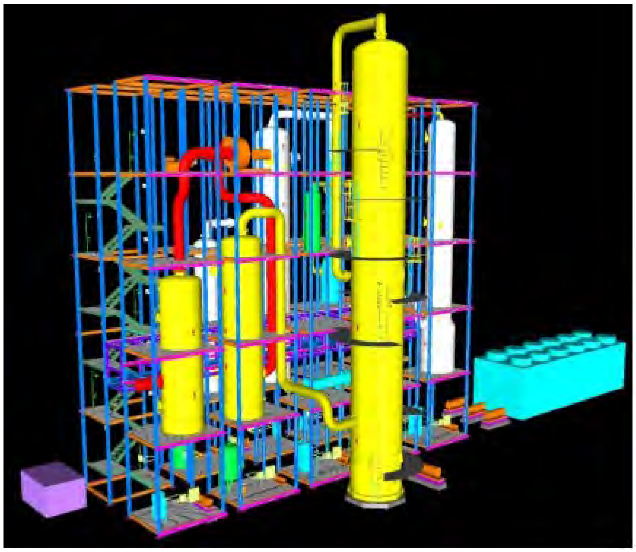

Figure 9: 10 MWe facility general layout.

Techno-Economic Analysis Findings

The preliminary TEA conducted and experimentally validated under FE0007395 shows that application of the improved process cycle (with MEA as the solvent) would reduce the COE by about 8% over the conventional 90% Reference Capture Case 10, and that use of H3-1 in the improved process cycle would reduce COE 12%. The TEA was updated to include discretized packing for absorber temperature control, a solids-incorporated solvent recovery system, split rich primary stripper feeds to reduce H_2O/CO_2 ratio in the stripper outlet, and de-superheating the carbon capture and storage (CCS) extracted steam with a feed water heater. In this case, the overall reduction in COE is 19%. Figure 10 shows that the cost of CO_2 capture (excluding transportation, storage, and monitoring) is reduced from $56.52 to $34.51 per tonne of CO_2 captured, a reduction of 38.9% with coal being the sole energy source. The cost of CO_2 capture could be further reduced to $25.26 per tonne of CO_2 captured when all auxiliary electricty and steam required for the carbon capture system are from natural gas-fuel by taking advantage of the low capital cost of natural gas combined electricity and heat unit.

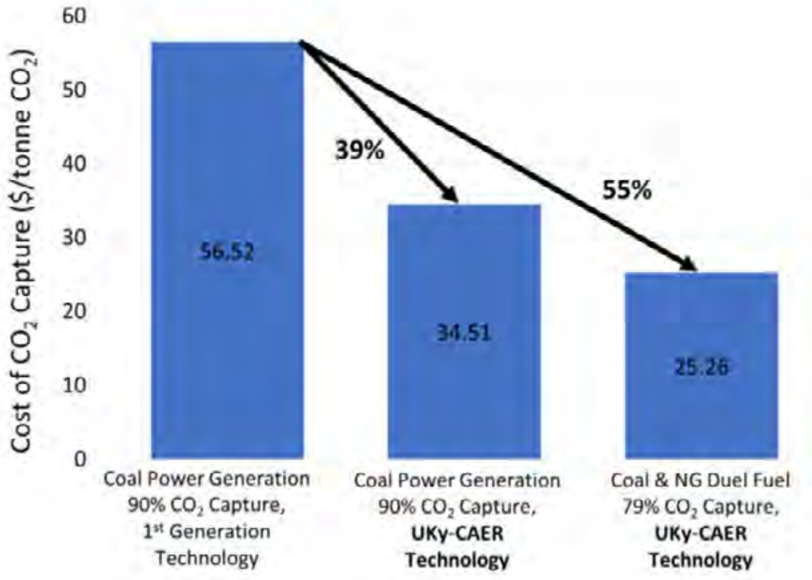

Figure 10: Cost of CO_2 capture estimates from techno-economic analysis.

However, additional cost reductions will be necessary to attain ultimate U.S. Department of Energy (DOE) program targets. For this, UK CAER estimates that a combination of a further-improved third-generation solvent will be critical, combined with absorption enhancement technologies via optimal absorber temperature profile and gas-liquid interface mixing. To illustrate the issue that current second-generation solvents are, generally, simply too expensive compared to conventional MEA, Table 1 shows the costs associated with MEA compared with two fictious Solvents A and B. Solvent B is 10 times the cost of MEA on a unit basis. In these cases with hypothetical solvents A and B assumed to be commercially available, the energy cost savings (due to lower energy consumption) associated with using solvents A and B are less than the additional solvent makeup cost.

TABLE 1: SOLVENT COST COMPARISON OF MEA WITH HYPOTHETICAL SOLVENTS A AND B

	30 wt% MEA	Solvent A	Solvent B
Make-up Rate (kg/ton CO_2)	1.5	0.5	0.5
Energy Consumption Compared to 30 wt% MEA		30% less	40% less
Unit Cost ($/kg)	1.5	9	15
Solvent Cost ($/tonne CO_2 Captured)	2.25	4.5	7.5
COE ($/MWh)	106.5	93.3	91.2

TABLE 2: CAER ADVANCED SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	<90	<90
Normal Boiling Point	°C	160–165	160–220
Normal Freezing Point	°C	-2	-2–5
Vapor Pressure @ 15°C	bar	$6.3x10^{-4}$	$6.3x10^{-4}$-$6.3x10^{-3}$
Manufacturing Cost for Solvent	$/kg	4–6 (estimated)	3–5
Working Solution			
Concentration	kg/kg	<0.45	<0.45
Specific Gravity (15°C/15°C)	-	1.01	1.01
Specific Heat Capacity @ STP	kJ/kg-K	3.5	3.5
Viscosity @ STP	cP	2.8 (fresh condition)	2.8 (fresh condition)

Surface Tension @ STP	dyn/cm	<55	<55
Absorption			
Pressure	bar	1	1
Temperature	°C	35-55	40
CO_2 Loading	mol/mol	0.46	0.51–0.55
Heat of Absorption	kJ/mol CO_2	<60	<60
Solution Viscosity	cP	4.3 (rich condition)	4-6
Desorption			
Pressure	bar	3.1	3.0
Temperature	°C	125	120
CO_2 Loading	mol/mol	0.23	0.30
Heat of Desorption	kJ/mol CO_2	<75	<75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate @ 10 MWe equivalent	kg/hr	43,000	
CO_2 Recovery, Purity, and Stripper Pressure	%/%/bar	90 99.9 3.0	
Absorber Pressure Drop	bar	<0.1–0.15	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~200	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Surface Tension – The tension of the surface film of a liquid caused by the attraction of the particles in the surface layer by the bulk of the liquid, which tends to minimize surface area. This is measured in force per unit length (dyn/cm).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted otherwise, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption reactions for any amine-based system can be broken into two primary reactions, as depicted in Figure 11. The absorption of CO_2 is primarily dictated by the reactions of primary amine (SC) to form carbamates. The reaction second order rate constant for these species can vary, but is generally on the order of (10^3 l/mol·s), with similar rate constants observed for the CAER solvent. The SC reaction generates a mole of proton for each mole of CO_2 captured, leading to primary amines being generally limited on a molar basis to 0.5 CO_2:1N. The CAER amine solvent utilizes a primary amine as the main component. Additionally, another minor component is added to the solvent to principally act as a proton receiver (PC) in the solution to balance the bicarbonate formation. The pKa of this proton receiver is higher (more basic) than that of the main component. The reaction from the proton receiver to directly form bicarbonate is much slower (100x). It is expected to function similarly to those enzymes in directly catalyzing the reaction of dissolved CO_2 in solution to form bicarbonate. A third reaction to form bicarbonate directly from hydroxide present in solution can generally be excluded from consideration despite the fast rate constant (10^4 l/mol·s) because hydroxide concentration is limited by the base dissociation constant in typical amine solutions ($<1 \times 10^{-4}$).

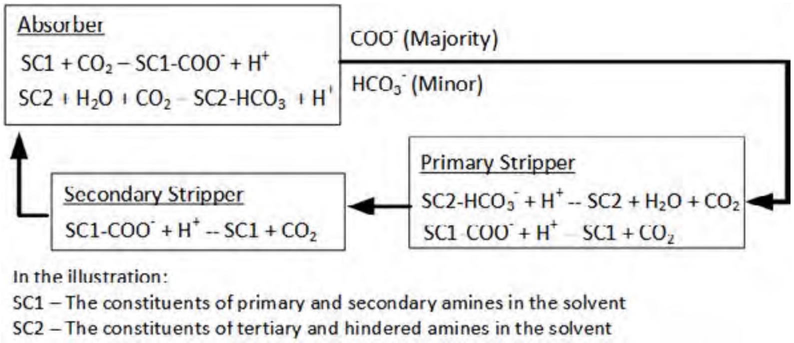

Figure 11: Schematic for reactions occurring in the CO_2 capture cycle.

Solvent Contaminant Resistance – The CAER solvent shows behavior analogous to MEA towards oxidation and flue gas components. Similar levels or less of oxidation and degradation due to flue gas components are anticipated.

Solvent Foaming Tendency – The addition of anti-foam to solvent can help control foaming tendencies by lowering the solvent surface tension. Any new solvent additive will need to be evaluated for its foaming potential and any that may increase foaming tendency should be avoided. The CAER solvent has very low foaming tendencies (less than 30% MEA) due to a low surface tension of <40 dyn/cm.

Flue Gas Pretreatment Requirements – Coal-fired power generation flue gas exiting from existing environmental controls is further polished to below 10 ppm SO_2 through an additional pretreatment step to slow the accumulation of sulfate in the solvent. Sulfate is an HSS, meaning it cannot be thermally removed from the solvent. Its accumulation will slowly reduce the CO_2 capture capacity of the solvent. If SO_2 is not present in the flue gas - for a natural gas combined cycle (NGCC) application, for example - additional pretreatment may not be required.

Solvent Makeup Requirements – Long-term stability is an ever-present concern of all solvent developers. The CAER solvent is composed of amines that are inherently more stable than MEA and has a higher thermal stability than MEA. As seen in Figure 12, a 50 to 70% decrease in rate-of-amine loss as a percent of initial is observed at the high temperatures associated with stripper conditions over a two-week period. Regression of the data compared to reference MEA predicts a thermal degradation rate similar to MEA at a 10°C higher stripper operating temperature. It is expected that the makeup requirements will be similar to that of MEA under the proposed process conditions of a higher stripper temperature/pressure.

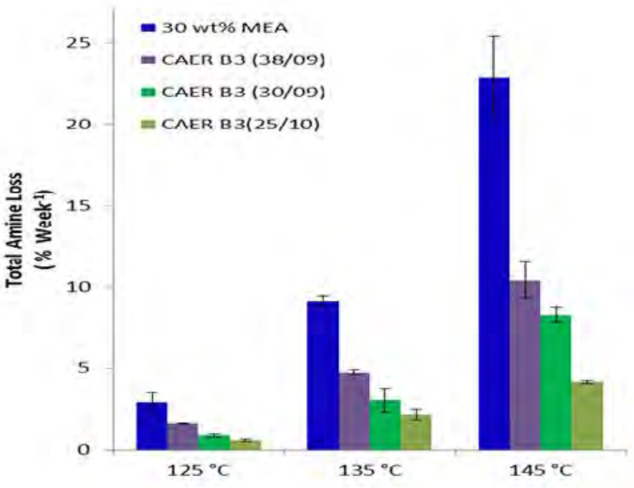

Figure 12: Rate of amine loss as total percent amine under stripper conditions of 30 wt% MEA (blue) and various combinations of CAER-B3.

Waste Streams Generated – The waste streams generated from the process are the spent soda ash solution and the CO_2 capture solvent, used for SO_2 removal and the absorption of CO_2, respectively. The loss of performance and how quickly the solvent is spent is impacted by the rate of degradation and HSS formation in the solvent. In practice, the solvent will be treated in a thermal reclaimer to remove HSSs and metal species, which will also produce a waste that is likely hazardous in nature.

Process Design Concept – The process flow is shown in Figure 1. In brief, the SO_2-polished flue gas (from the pretreatment tower) enters the CO_2 pre-concentrating membrane, if applied, to produce two streams that are injected into the CO_2 absorber at separate locations. If the CO_2 pre-concentrating membrane is not applied, the flue gas enters the bottom of the absorber after pretreatment. After gaseous CO_2 is converted into aqueous carbon species, the carbon-rich solution exits the absorber bottom, is pressurized, and sent to the rich-lean solution heat exchanger (Crossover HXER) with split rich outlets to primary stripper. The hot rich stream from lean/rich heat exchanger enters the dewatering membrane unit, if applied, for solution pre-concentration, which is not shown in Figure 1. The permeate stream of the dewatering membrane unit with low amine concentration combines with the regenerated lean solution stream exiting at the outlet of the stripper. The reject stream, which has higher carbon loading than the feed stream, is sent to the middle of pressurized stripper for solvent regeneration. If the dewatering membrane unit is not applied, the hot rich stream leaving the lean/rich heat exchanger is fed directly to the middle of the pressurized stripper. The warm rich stream is fed to the top of the pressurized stripper. This stage will require an energy source to drive the reboiler. At the stripper exit, the gas stream consists primarily of CO_2 and water vapor at a pressure of approximately 3 bar. After exiting the heat recovery unit at the top of stripper, the CO_2 gas stream has a purity of 99.9% and will be pressurized to about 135 bar and intercooled for downstream utilization or storage. The carbon-lean solution exiting the primary stripper is sent to the lean/rich heat exchanger, where heat will be recovered with the carbon-rich solution. After the lean/rich heat exchanger, this heat depleted stream will be cooled to approximately 40°C and recycled to the absorber.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value
Cost of Carbon Captured	$/tonne CO_2	$31.95 (Excluding TS&M) $43.08 (Including TS&M)
Cost of Carbon Avoided	$/tonne CO_2	$37.00 (Excluding TS&M) $49.22 (Including TS&M)
Capital Expenditures	$/MWhr	$$64.93 (Fixed + Capital Costs) $52.98 (Capital Cost only)
Operating Expenditures	$/MWhr	$ 41.24 (Fuel + Variable Costs) 11.36 (Variable Cost Only)
Cost of Electricity	$/MWhr	$106.17 (Excluding TS&M) $114.50 (Including TS&M)

*All values are in 2011$

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in Table 3 are based on the reference plant provided by NETL for TEA analysis, found in the *"Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity"* report, Rev. 2a.

Scale of Validation of Technology Used in TEA – The TEA analysis was validated at the 0.7 MWe small pilot scale.

Qualifying Information or Assumptions – No qualifying information or assumptions are noted.

technology advantages

- Cost-effective approach to capture CO_2 from utility coal-fired units that can be applied with most advanced solvents.
- The two-stage stripping unit, including the deployment of an air-based secondary stripper, will regenerate an exceptionally CO_2-lean solvent, increasing the rate of CO_2 absorption and solvent cyclic capacity, will eliminate the need for deionized water for amine loop makeup, and will provide a direct cooling effect on lean solvent prior to returning to the absorber.
- Low capital cost resulting from a discretized packing arrangement and in-situ gas-liquid distribution to minimize the liquid maldistribution.
- High system efficiency resulting from carbon capture system internal heat integration, rich solvent split to the primary stripper, and de-superheating extracted steam by splitting the feed water.
- The solvent recovery column, at the outlet of the gas stream leaving the CO_2 absorber, with solid particle assistance to minimize the solvent emissions, minimizing solvent makeup requirements.
- The advanced solvent used in this system has: (1) a higher mass-transfer flux; (2) a higher net cyclic carbon capacity; (3) less energy demand for CO_2 stripping; and (4) lower corrosion rates than a 30 wt% MEA solution, leading to lower capital and operational costs.
- The advanced solvent also has a 15 to 20% lower degradation rate compared to 30 wt% MEA, leading to lower solvent makeup volume.

- Potential for reduced capital cost for post-combustion CO_2 capture, chiefly through increased absorption kinetics that allow for a smaller absorber and regeneration columns coupled with a lower solvent circulation rate and smaller associated equipment (blowers, pumps, and piping systems) and lower steam extraction requirement due to stripper intensification which leads to a smaller power generation unit requirement.
- Potential for reduced energy consumption compared to conventional MEA-based scrubbing, chiefly attributable to:
    - High cyclic capacity.
    - High stripper pressure: the primary CO_2 stripper can be operated at approximately 3 bar in order to maximize the energy benefit while minimizing system capital and solvent degradation, which could lead to low compressor capital and operating costs.
    - Heat integration to power air-based secondary stripper.

R&D challenges

To achieve the targets set forth by DOE/NETL, several R&D challenges remain to be met.

- Due to the low CO_2 absorption driving force in utility flue gas and the highly viscous nature of second-generation + solvents, the low-pressure drop structured packing suffers from a lack of macro-mixing/turbulence between the bulk solvent and the gas-liquid interface, which results in localized channel flow and significantly reduces column effectiveness. The application of in-situ liquid distributors could re-adjust the pressure and redistribute the liquid within a section of structured packing, while keeping the total column height at a minimum.
- Two-stage solvent regeneration has been successfully demonstrated at the small pilot scale, but intensification in the absorber and strippers can be applied to reduce the column height and steam requirement.
- The UK CAER solvent recovery from the absorber exit gas stream has been demonstrated at lab, bench, and pilot scale.
- Use of a CO_2 pre-concentrating membrane in the absorber flue gas feed has been demonstrated at bench scale, and tested at the pilot scale.
- Implementation of a smart process control scheme needs to be demonstrated to reduce the solvent regeneration energy while also responding quickly to the dynamic load and ambient conditions.
- Waste minimization techniques need to be demonstrated at the large pilot scale. Accumulation of elements such as selenium (Se) and arsenic (As) in the CO_2 capture solvent can result in a hazardous classification of the material.
- The relationship between thermal compression and lean/rich heat exchanger size needs to be understood and included when reporting solvent and process performance. It is generally accepted that the stripper is equilibrium-controlled, and in-situ thermal compression via high-temperature operation will drop the H_2O/CO_2 ratio at the stripper outlet, lowering the specific reboiler duty. The 0.7-MWe small pilot experimental data indicate this holds true only for systems with a relatively large lean/rich heat exchanger (low ΔT between hot lean from stripper and hot rich to stripper).
- Long-term, low-cost advanced solvent performance needs to be demonstrated. While several solvents are currently in use at the commercial scale, they are costly, and improved performance may not justify this cost.
- Lower-cost corrosion-resistant materials of construction need to be demonstrated. In general, most amine solvents have the tendency to corrode metal surfaces, especially in high carbon loading and/or high temperature locations. Sections of the CCS that are specifically impacted are the absorber bottom, lean/rich heat exchanger, and the top of the stripper. Currently, most CCS systems deployed in the utility environment use stainless steel for locations where wetted surfaces are expected, while some are using concrete with a plastic/polymer or ceramic liner for the CO_2 absorber, which results in a higher capital investment.

status

The project was completed in May 2021, including Phase I (Feasibility) and Phase II (Design). In Phase I of FE0031583, the host site for the proposed large-scale pilot was selected as Wyoming Integrated Test Center, a test facility located within Basin Electric Power Cooperative's Dry Fork Station coal-fired power plant near Gillette, Wyoming, wherein flue gas from the plant is diverted to the testing facility. Preliminary engineering and cost estimates were prepared for the equipment inside the battery limit (ISBL) and outside the battery limit (OSBL). A NEPA contractor was also selected, and a comprehensive environmental information volume was completed with no significant EH&S impacts anticipated.

In Phase II of FE0031583, the FEED study was conducted with process development packages developed for the ISBL and OSBL systems. Utilizing NETL's Institute for the Design of Advanced Energy Systems (IDAES), a feedforward control scheme was developed and optimized to reduce the capture system response time to power plant load changes. In addition, an aerosol emissions model was developed for the advanced solvent, and the output from the model will inform the design of the solvent recovery system for optimized emissions control. A process hazard and operability analysis (HAZOP) was performed covering both ISBL and OSBL preliminary process development packages to identify potential system hazards and operational problems. The NEPA process was completed with application to Wyoming Department of Environmental Quality (WDEQ) for all required environmental permits.

available reports/technical papers/presentations

FE0031583

Liu, K., et. al., "UKy-CAER Heat-integrated Transformative CO2 Capture Process in Pulverized Coal Power Plants," presented at the 2020 NETL Integrated Project Review Meeting – CCUS Integrated Projects, August 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Liu.pdf.*

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Nikolic, H., et. al., "UKy-CAER Heat-integrated Transformative CO_2 Capture Process in Pulverized Coal Power Plants," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKCAER-Heat-Integrated-CO2-Capture.pdf*.

"UKy-CAER Heat-integrated Transformative CO_2 Capture Process in Pulverized Coal Power Plants," Project kickoff meeting presentation, May 2018. *https://www.netl.doe.gov/project-information?p=FE0031583*.

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Commercial Carbon Capture Design and Costing: Part Two (C3DC2)

primary project goal

ION Clean Energy Inc. (ION), Nebraska Public Power District (NPPD), and their partners conducted a front-end engineering design (FEED) study for a carbon capture system designed for retrofit onto Unit 2 of NPPD's Gerald Gentleman Station (GGS2), a 700-megawatt (MW) coal-fired power station located in Western Nebraska. For the project, a 700-MW-equivalent (two parallel 350 megawatt-electric [MWe] capture units) commercial-scale carbon dioxide (CO_2) capture plant was designed and costed for GGS2. A hazard and operability (HAZOP) study was included with this analysis. Finally, an investigation of biomass co-firing was performed with the goal of achieving net-zero or net-negative carbon emissions (performed as a sensitivity study).

technical goals

The overall project objective was to conduct a FEED study for a commercial-scale CO_2 capture system retrofitted onto an existing coal-fueled Rankine cycle power station. With this approach, the team strove to decarbonize as much of Unit 2 as possible utilizing ION's ICE-21 solvent technology. This project leveraged prior U.S. Department of Energy (DOE) project award FE0031595, which conducted a design and costing study for a 300-MW slipstream carbon capture system for GGS2.

technical content

The project team designed the capture system and produced a capital cost estimate that would cover both the engineering design for the carbon capture process and the balance of plant. The engineering design was performed at a level consistent with an Association for the Advancement of Cost Engineering (AACE) Class 2 estimate, which would result in a capital cost accuracy range of -15 to +20%. The FEED study was based off of an integrated design at NPPD's Gerald Gentleman Station's Unit 2, which would utilize a two-unit, 350-MW train design for the CO_2 capture system. The project will utilize ION's ICE-21 solvent technology, a carbon capture process comparable to a standard temperature-swing chemical absorption scheme (such as monoethanolamine [MEA]), with the following key differences in design:

- Cold-rich bypass to control stripper temperature and reduce required heating steam.
- Optimized lean/rich cross exchanger (LRXC) design.
- Sulfur dioxide (SO_2) polishing via sodium hydroxide (NaOH) to reduce total sulfur emissions.
- Optimized CO_2 compressor selection.

A schematic of the CO_2 capture process is shown in Figure 1.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent Technology Retrofit to Coal-Fired Power Plant

participant:
ION Clean Energy Inc.

project number:
FE0031840

predecessor project:
FE0031595

NETL project manager:
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partners:
Nebraska Public Power District; Sargent & Lundy; Koch Modular Process Systems; Siemens

start date:
10.01.2019

percent complete:
100%

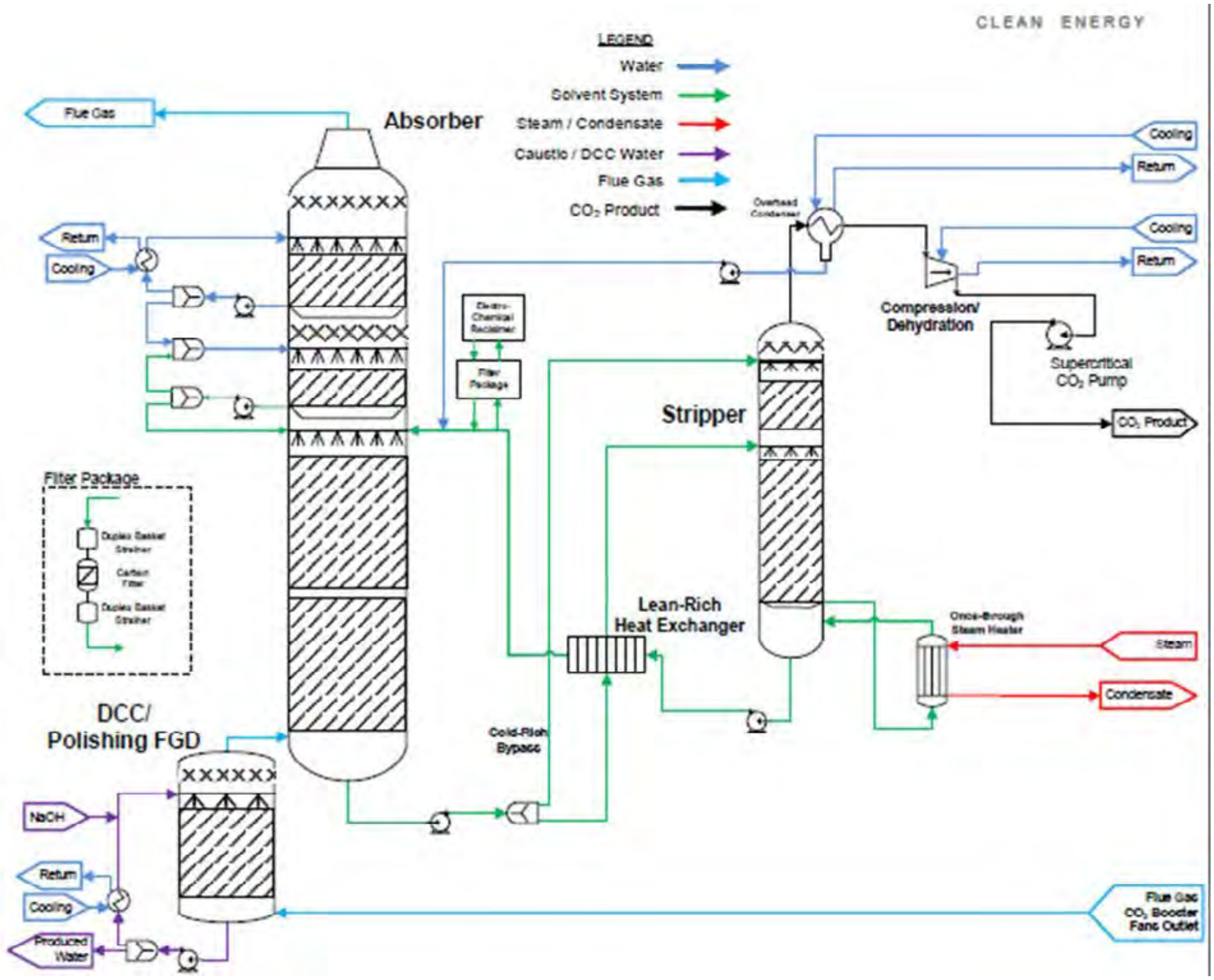


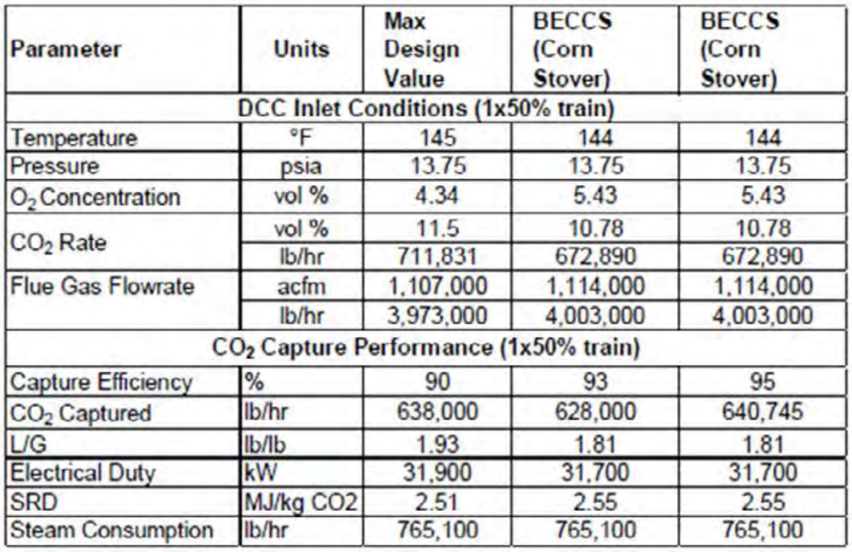
Figure 1: Carbon capture system design.

The FEED study produced process flow diagrams; utility flow diagrams; piping and instrument diagrams; heat and material balances; a 3D model; plot plans; final layout drawings; complete engineered process and utility equipment lists; one-line diagrams for electrical, electrical equipment, and motor schedules; vendor quotations; detailed project execution plans; and resourcing and workforce plans developed by the project team. Balance of plant engineering design included specifications for utilities, such as compression, cooling water, and waste treatment, as well as the sources of electricity and steam necessary to power the capture process. Civil and structural engineering tasks were also incorporated throughout the design to include the proper stormwater runoff and spill containment, as well as geological assessments to support foundation design.

The team conducted a series of studies and investigations to aid in the design of the carbon capture facility, including steam sourcing, cooling water system, solvent materials compatibility, wastewater treatment, permitting and regulatory review, reagent handling, constructability review, overpressure relief, and project execution and operations management planning.

In addition, the project team incorporated a sensitivity study for biomass using corn stover pellets (bioenergy with carbon capture and storage [BECCS]) to assess the potential for net-zero or net-negative carbon emissions. The pellets were delivered by truck to a retrofitted gasifier unit. The syngas produced by the gasifier was then used to co-feed the coal boiler. The CO_2 capture performance results of this study are shown in Table 1, where the as-designed CO_2 capture facility would result in a 93% capture rate of CO_2 in the BECCS case but could be increased to 95% capture with the addition of more plates in the LRXC.

TABLE 1: BECCS PERFORMANCE RESULTS



Parameter	Units	Max Design Value	BECCS (Corn Stover)	BECCS (Corn Stover)
DCC Inlet Conditions (1x50% train)				
Temperature	°F	145	144	144
Pressure	psia	13.75	13.75	13.75
O_2 Concentration	vol %	4.34	5.43	5.43
CO_2 Rate	vol %	11.5	10.78	10.78
	lb/hr	711,831	672,890	672,890
Flue Gas Flowrate	acfm	1,107,000	1,114,000	1,114,000
	lb/hr	3,973,000	4,003,000	4,003,000
CO_2 Capture Performance (1x50% train)				
Capture Efficiency	%	90	93	95
CO_2 Captured	lb/hr	638,000	628,000	640,745
L/G	lb/lb	1.93	1.81	1.81
Electrical Duty	kW	31,900	31,700	31,700
SRD	MJ/kg CO2	2.51	2.55	2.55
Steam Consumption	lb/hr	765,100	765,100	765,100

The final report summarized project results from the FEED study, including a systems and benefits analysis, summarized the results from the technical and economic feasibility analysis of scale-up, and made recommendations for future research and development (R&D). The operating parameters of the capture system's design is given in Table 2.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	75–95
Normal Boiling Point	°C	150–210
Normal Freezing Point	°C	-15–2
Vapor Pressure @ 15°C	bar	$1\text{-}2 \times 10^4$
Manufacturing Cost for Solvent	$/kg	Proprietary
Working Solution		
Concentration	kg/kg	0.6–0.85
Specific Gravity (15°C/15°C)	—	0.9–1.2
Specific Heat Capacity @ STP	kJ/kg-K	2–3
Viscosity @ STP	cP	<5
Absorption		
Pressure	bar	1.0–1.15
Temperature	°C	20–50
Equilibrium CO_2 Loading	mol/mol	0.4–1.0
Heat of Absorption	kJ/mol CO_2	50–100
Solution Viscosity	cP	<20
Desorption		
Pressure	bar	1.1–1.8
Temperature	°C	80–150
Equilibrium CO_2 Loading	mol/mol	0.01–0.40
Heat of Desorption	kJ/mol CO_2	50–100

Finally, Table 3 shows the accomplished economic performance data from the study and the comparison with previously established R&D targets.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.97	30.00
Capital Expenditures	\$/MWhr	22.80	21.00
Operating Expenditures	\$/MWhr	14.03	12.00
Increase in Cost of Electricity	\$/MWhr	36.83	33.00

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced

Increase in Cost of Electricity – Projected additional cost of electricity per unit of energy produced under expected operating conditions for the addition of CO_2 capture process

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

LRXC – Lean/Rich Cross Exchanger. A heat exchanger that connects the lean and rich solvent streams that further cools the lean solvent while heating the rich solvent, increasing absorption and desorption efficiencies.

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – Estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	150	10.5	20.5	66.4	5.3	0.80	15	150

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The physico-chemical properties of ION's solvent system allow for a unique mechanism that combines fast kinetics with low energy consumption.

Solvent Contaminant Resistance – Sulfur oxides (SO_X) and nitrogen oxides (NO_X), other than nitric oxide (NO), are absorbed into the solvent and lower the carrying capacity of CO_2. Oxidative and thermal degradation are manageable. To date, ION's solvent system has not been limited by contaminant concentration.

Solvent Foaming Tendency – No foaming issues have been seen during either of ION's solvent pilot test campaigns.

Flue Gas Pretreatment Requirements – It is preferred that the flue gas be saturated with water vapor and can include any concentration of CO_2. Pretreatment to levels of SO_X less than 10 to 30 parts per million (ppm) (spikes are manageable) and NO_X less than 100 to 200 ppm is also favored.

Solvent Makeup Requirements – Proprietary.

Waste Streams Generated – Proprietary.

Process Design Concept – ION's solvent-based process steps include pre-scrubbing to remove SO_X, several other gases, and most of the particles; a direct contact cooling unit to control the inlet flue gas temperature and humidity; an absorber consisting of a packed column with counter-flow for removal of CO_2 into the proprietary solvent; and water wash to remove solvent droplets and vapors from the exhaust gas. Following the absorption step, the final unit operation is a regenerator to produce the CO_2, recover the solvent, and recycle the solvent back to the absorber.

technology advantages

As part of the FEED study, the proprietary ION ICE-21 solvent technology was utilized. Relative to aqueous MEA technology and other commercial capture systems, ION's ICE-21 solvent technology offers the following benefits to lower operating and capital costs for CO_2 capture:

- Reduction in regeneration energy requirements.
- Higher CO_2 loading capacities.
- Reduced corrosion and solvent losses.
- Faster absorption kinetics.
- Less water used by the process.

The carbon capture plant was designed to take full advantage of these benefits, which resulted in a smaller physical plant, reduced energy requirements, less solvent degradation, lower emissions, and lower capital costs relative to systems built with the DOE Bituminous Baseline Study case benchmark solvents.

R&D challenges

In the project, ION looked to optimize the operating costs versus the capital costs, which were defined by some design basis decisions such as sparing philosophy, process robustness, and maintenance.

status

The project has concluded. The results show that the process with 10% biomass syngas feed can achieve a 98% overall reduction in CO_2 emissions compared to a fully coal-powered plant without carbon capture and storage (CCS). More than 100% net reduction (carbon-negative) can be achieved through higher packing and a more optimized LRXC.

available reports/technical papers/presentations

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Full-Scale FEED Study for Retrofitting the Prairie State Generating Station with an 816-MWe Capture Plant Using Mitsubishi Heavy Industries America Post-Combustion CO_2 Capture Technology

primary project goal

The University of Illinois and its partners performed a front-end engineering design (FEED) study for the retrofit of the Prairie State Generation Company's (PSGC) coal-fired power station with post-combustion carbon capture. The University of Illinois and the project team produced a FEED study that used Mitsubishi Heavy Industries' (MHI) Advanced Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ to retrofit one of PSGC's two generating units (approximately 816 megawatt-electric [MWe]) in Marissa, Illinois, to become the largest post-combustion carbon dioxide (CO_2) capture plant in the world.

technical goals

- The purpose of the FEED study was to complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at PSGC.
- The team performed multiple feasibility and design studies in preparation for developing engineering deliverables. These studies helped define the scope of the retrofit project, based on the technology, site, and client needs.
- Once the scope was defined, detailed design commenced for the CO_2 capture system and its integration with the existing facility. Various design and engineering deliverables were developed that helped define commodity quantities, equipment specifications, and labor effort required to execute the project.

technical content

The overall project goal was a full FEED study on a carbon capture system for Unit #2 (816 MWe) at the PSGC Energy Campus in Marissa, Illinois, based upon on the KM CDR Process CO_2 capture technology from MHI. This capture technology represents the current state-of-the-art and employs an improved solvent from that used at the 240-MWe Petra Nova capture plant in Thompsons, Texas. The capture technology was scaled-up to 816 MWe.

Work on this FEED study produced detailed engineering designs, costing, and timelines for the construction. It also designated permitting agencies and timelines in order to execute the follow-on build and operation of the project. Lessons learned during the FEED study were documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Amine-based Advanced KM CDR Process Retrofit to Coal-Fired Power Plant

participant:
University of Illinois at Urbana-Champaign

project number:
FE0031841

NETL project manager:
Carl Laird
carl.laird@netl.doe.gov

principal investigator:
Kevin O'Brien
University of Illinois at Urbana-Champaign
kcobrien@illinois.edu

partners:
Mitsubishi Heavy Industries Ltd.; Prairie State Generating Company; Kiewit Engineering Group Inc.; Sargent & Lundy

start date:
10.01.2019

percent complete:
100%

The KM CDR Process is an improvement upon MHI's original KM CDR Process and is an amine-based CO_2 capture process that uses a newly developed solvent known as KS-21. The CO_2 capture system can recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.

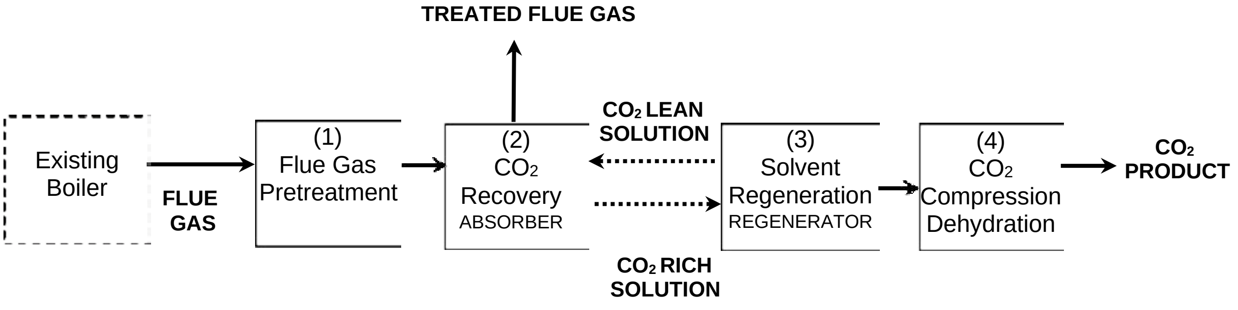

Figure 1: Block flow diagram of the CO_2 recovery plant.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of sulfur dioxide (SO_2) in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

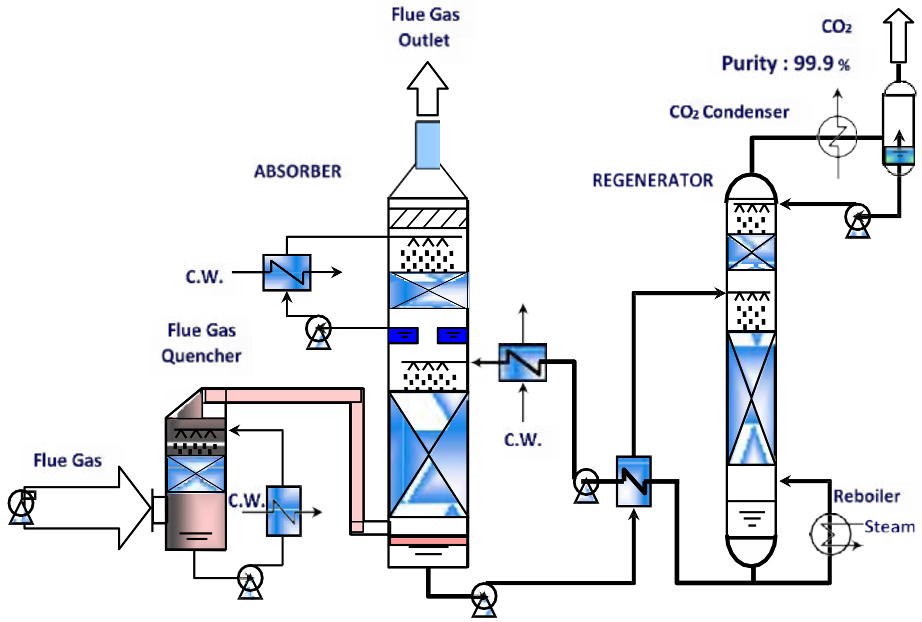

Figure 2: Carbon capture basic process flow diagram.

In solvent regeneration, cool rich solvent is heated by the hot lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current Project Value	Target Project Value
Cost of Carbon Captured	\$/tonne CO_2	43.42	45
Cost of Carbon Avoided	\$/tonne CO_2	54.29	—
Capital Expenditures	\$/MWhr	24.5	—
Operating Expenditures	\$/MWhr	27.3	—
Cost of Electricity	\$/MWhr	N/A	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Includes costs incurred during the construction phase and throughout the life of the project, including costs to finance the project through construction and debt service through the operation of the plant. Calculation methodology follows NETL-PUB-2263B “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity” (Rev. 4), with capital expenditure and operational expenditure costs developed during the FEED study implemented where available. Cost of Electricity (COE) calculations are not considered as the new CO_2 capture facility is not a source of power.

Scale of Validation of Technology Used in TEA – Large-scale capture retrofit (816 MWe).

Qualifying Information or Assumptions –

- Included in cost calculations:
    - Capital costs developed during the FEED study.
    - Operating costs developed during the FEED study.
    - Owner costs.
    - 90% capacity factor.
    - Fixed charge rate: 0.0661.**
- Not included in cost calculations:
    - Taxes.
    - Insurance on operating facility.
    - CO_2 Transport & Storage (T&S) costs.
    - Site-specific costs*.
    - Costs associated with construction or operation of the existing PSGC coal-fired power station.

* Capital cost has been normalized by removing \$155 million of site-specific costs to allow for comparison to generic cost assessments (e.g., 15-mile pipeline routing cooling tower blowdown to an outfall structure).

Land, permitting costs, legal fees, owners engineer costs, owner contingency, and financing costs are approximated as 10% of total project cost. NETL-PUB-22580 “Cost Estimation Methodology for NETL Assessments of Power Plant

Performance" (February 2021) indicates 17.7% (15% + 2.7%) as typical, based on an engineering, procurement, construction, and management (EPCM) model and including FEED study costs; 10% used due to engineering, procurement, and construction (EPC) being the expected delivery model (labor/material risk already carried in contractor cost) and the project having already completed the FEED study.

** The financial structure for debt-to-equity split, cost of debt, and return on equity (ROE) is based on a real rates financial structure for investor-owned utility from NETL-PUB-22580 "Cost Estimation Methodology for NETL Assessments of Power Plant Performance" (February 2021). Spending nominally distributed over the four-year capital expenditure period (10%/40%/30%/20%).

technology advantages

- Used an improved, newly developed proprietary solvent known as KS-21. This solvent's properties translate into reduced capital costs.
  - Has less volatility, which reduced the height of the water wash section of the CO_2 absorber, lowering capital cost.
  - Has improved thermal stability, allowing the regenerator to be operated at a higher pressure and temperature, thereby reducing the equipment size and the power consumption for CO_2 compression, resulting in lowering operating and capital costs.
  - More resistance to oxidative degeneration, which reduces solvent loss.
  - Has lower heat of absorption, which allows higher circulation rate and therefore slightly less steam consumption.
- Can recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.
- The capture system was scaled up using multiple trains so that it could be standardized and modularized, and so that the overall project cost could be reduced.

R&D challenges

- To deploy the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large-scale (17,000–23,000 metric tonnes per day).

status

Reports were completed and submitted during the duration of the project, including the design basis document, utility requirements, detailed engineering document, hazard and operability (HAZOP) review, watershed impact report, constructability review, cost assessment, and regulatory and permitting pathway/analysis reports. The final FEED study package was completed and submitted.

available reports/technical papers/presentations

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," November 13, 2019. Presented by Kevin O'Brien, University of Illinois, NETL Project Kickoff Meeting. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10869&filename=Full-Scale+FEED+Study+For+a+816+MWe+Capture+Plant+at+the+Prairie+State+Generating+Company+Using+Mitsubishi+Heavy+Industries+of+America+Technology.pptx*.

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," August 17, 2020. Presented by Kevin O'Brien, University of Illinois, 2020 NETL Project Review Meeting - CCUS Integrated Projects. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_OBrien.pdf*

"Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology," August 2, 2021, Presented by Kevin O'Brien and Jason Dietsch, University of Illinois, 2021 NETL Carbon Management Research Project Review Meeting. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_OBrien.pdf*

“Full-Scale FEED Study for a 816 MWe Capture Plant at the Prairie State Generating Company Using Mitsubishi Heavy Industries of America Technology” January 5, 2022. Presented by Kevin O'Brien, University of Illinois, Final Project Briefing. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12602&filename=Full-Scale+FEED+Study+for+a+816+MWe+Capture+Plant+at+the+Prairie+State+Generating+Company+Using+Mitsubishi+Heavy+Industries+of+America+Technology.pdf*.

Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant

primary project goal

Electric Power Research Institute (EPRI) and its partners Fluor Corporation and California Resources Corporation (CRC) are conducting a front-end engineering design (FEED) study to determine the technical and economic feasibility of a retrofit, post-combustion carbon capture technology on a commercially operating, natural gas-fired combined cycle (NGCC) power plant.

technical goals

Conduct a FEED study for 75% overall capture (90% capture on 83% slipstream) at CRC's 550-megawatt-electric (MWe) NGCC Elk Hills Power Plant (EHPP) using Fluor's proprietary Econamine FG Plus^{SM} (EFG+) aqueous amine technology. The captured 4,000 tonnes of carbon dioxide (CO_2) per day will be used by CRC for enhanced oil recovery (EOR) in fields adjacent to the power plant.

technical content

The FEED study will examine the cost and engineering requirements for installing a plant to capture CO_2 produced by the 550-MWe NGCC unit located in the Elk Hills Oil Field in Kern County, California. Fluor is the design engineering contractor and Fluor's EFG+ technology is used for the carbon capture system design. CRC is the owner and operator of the host site, EHPP. Fluor's EFG+ technology is a post-combustion CO_2 capture technology with proven process for removal of CO_2 from flue gases, with the CO_2 product used for EOR and other applications.

The FEED study deliverables will include a design basis, process flow diagrams, piping and instrument diagrams, equipment datasheets, a plot plan, bulk material takeoffs, and a capital cost estimate. For the design basis of the FEED study, the completed and ongoing details include: consolidated historic performance and run history of the power plant, evaluating various operating scenarios and conditions; results from flue gas testing review and validation of solvent performance through FEED; historic construction details from surrounding facilities to incorporate site requirements; ongoing review and optimization of energy use and waste streams; and ongoing evaluation of construction practices and contracting strategies to optimize cost, schedule, and risk.

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Econamine FG Plus^{SM} Retrofit to NGCC

participant:

Electric Power Research Institute, Inc.

project number:

FE0031842

NETL project manager:

Carl Laird
carl.laird@netl.doe.gov

principal investigator:

Abhoyjit Bhown
EPRI
abhown@epri.com

partners:

Fluor Corporation; California Resources Corporation

start date:

10.01.2019

percent complete:

100%

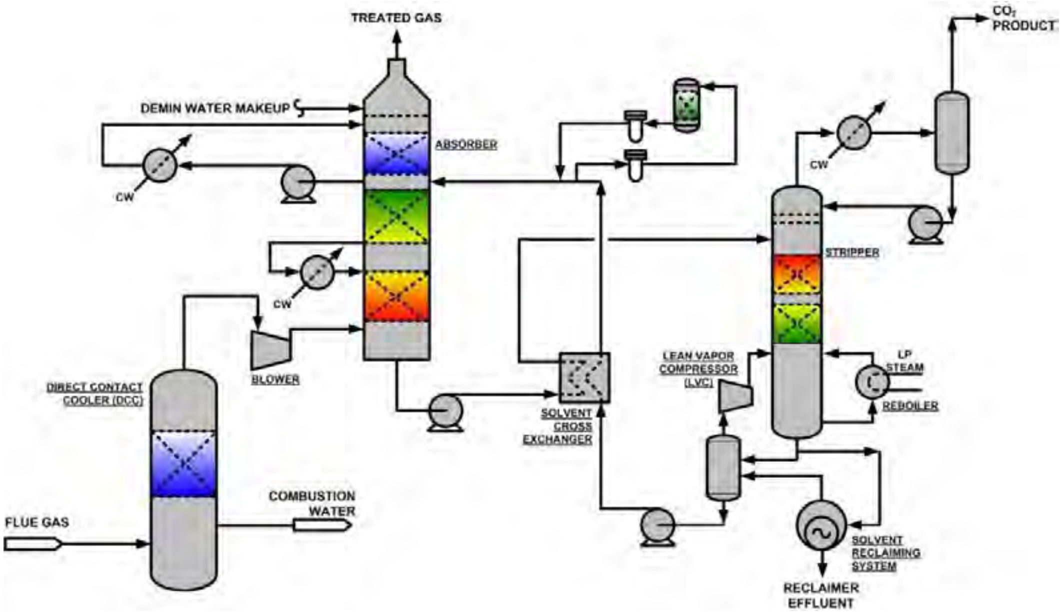

Figure 1: Simplified schematic of Fluor Corporation's Econamine FG Plus™ CO_2 capture process.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the NGCC unit (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	**Temperature** °F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.5	205	4.54	9.30	72.95	12.34	0.88	0.7	1.7

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is by chemical reaction.

Solvent Contaminant Resistance – The solvent has high resistance to contaminants in the flue gas due to the solvent maintenance system's ability to maintain the solvent in pristine condition.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – None.

Solvent Makeup Requirements – 0.42 kg/tonne CO_2.

Waste Streams Generated – Solvent maintenance system waste.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Proposed Module Design – To be prepared after logistics/route study.

technology advantages

- FEED studies for carbon capture systems at actual sites such as this will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.
- This FEED study could lead to the world's first commercial deployment of carbon capture on a natural gas-fired power plant and could be duplicated at other power plants across the world.

- Fluor's latest version of its EFG+ technology has several key features, including enhanced solvent formulation that has a high resistance to degradation, reduced amine circulation rate, a solvent maintenance system that keeps the solvent in pristine condition, low waste production, very low absorber vent emissions, and load-following capability. These features are proven on both gas turbine exhaust and coal flue gas. The enhanced dual-cell column and absorber design enables a large flue gas throughput, which reduces capital costs.

R&D challenges

- Targeting not just operating expenses, but also capital expenses in this FEED study to minimize the overall cost of CO_2 capture via utilization of various technology and process synergies.
- Optimizing cooling water usage as California and the Bakersfield area's ongoing challenge of water availability for power production.

status

The final FEED study package was completed and submitted to the National Energy Technology Laboratory (NETL). Design activities completed include process modeling, heat and material balances, process and utility flow diagrams, piping and instrumentation diagrams, equipment sizing and selection, process hazard analysis, cause and effect diagrams, plot plan, electrical load list, 3D model development, and capital and operating cost estimates. Value engineering studies were conducted to reduce the column heights of the direct contact cooler and absorber designs, reduce flue gas ducting costs using alternate geometry and metallurgy, and optimize the plot layout by reducing the size of the plate and frame exchanger support structure and minimizing the higher cost alloy piping. A study was also conducted to modify integration with the host power plant, allowing the existing steam turbine to supply the full regeneration steam requirement to the capture plant, thus eliminating the need for new natural gas-fired boilers dedicated to the capture plant, increasing CO_2 captured from the plant and reducing cooling tower load and water consumption. The final report is under development.

available reports/technical papers/presentations

"Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," DOE Project Kickoff Meeting, October 30, 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10875&filename=Front-End+Engineering+Design+Study+for+Retrofit+Post-Combustion+Carbon+Capture+on+a+Natural+Gas+Combined+Cycle+Power+Plant.pdf.*

"Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," 2020 NETL Project Review Meeting - CCUS Integrated Projects, August 18, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Bhown.pdf.*

"Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies, August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Bhown.pdf*.

Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station

primary project goal

The overall goal of this project is to perform a front-end engineering design (FEED) study for the retrofit of the San Juan Generating Station (SJGS) with post-combustion carbon capture. The FEED study will document the initial engineering and cost estimates for the retrofit project, including the levelized cost of carbon capture on an existing plant, and provide estimates of the technical and economic viability of extending the life of the existing SJGS coal-fired power plant through the installation of Mitsubishi Heavy Industries' (MHI) Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ carbon dioxide (CO_2) capture technology. The FEED study will enable SJGS to move forward into detailed engineering, procurement, installation, and operation in future work.

technical goals

- The purpose of the FEED study is to complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at SJGS.
- The team will perform multiple feasibility and design studies based on project-specific details in preparation for developing engineering deliverables. These studies will help define the scope of the retrofit project, based on project-specific decisions, technology-specific performance, site-specific requirements, and client-specific needs.
- Once the scope has been defined, detailed design will commence for the CO_2 capture system and its integration with the existing facility. Various design and engineering deliverables will be developed that will help define commodity quantities, equipment specifications, and labor effort required to execute the project.

technical content

Enchant and its partners will perform a FEED study for retrofitting the host site with an advanced amine-based carbon capture technology. The FEED study will be performed for 847 megawatts electric (MWe; Units 1 and 4 at SJGS in Waterflow, New Mexico). The coal is supplied by the adjacent mine, San Juan Coal Company, owned by Westmoreland Holdings. The current contract expires on June 30, 2022; however, San Juan Coal has offered SJGS a new contract in support of the plant's continued operation under decarbonization. Both operating units are equipped with state-of-the-art environmental controls that meet or exceed government-permitted levels of emissions for nitrogen oxide (NO_X), sulfur dioxide (SO_2), particulate matter (PM), and mercury (Hg), making the unit carbon capture-ready from an emissions perspective.

SJGS is currently owned by a group of public utilities and municipal power entities and is operated by Public Service of New Mexico (PNM), pursuant to the Amended San Juan Participation Agreement (ASJPA). The City of Farmington (Farmington), currently a part-owner and also sub-recipient under this award, has the right under the ASJPA to acquire the 95% interest in SJGS held by all the other owners

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Amine-Based KM CDR Process Retrofit to Coal-Fired Power Plant

participant:
Enchant Energy LLC

project number:
FE0031843

NETL project manager:
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Peter Mandelstam
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partners:
City of Farmington; Mitsubishi Heavy Industries America Inc.; Mitsubishi Heavy Industries Engineering Ltd.; Sargent and Lundy LLC; Navigant Consulting; EJM Associates LLC; Baker Tilly Virchow Krause LLP

start date:
10.15.2019

percent complete:
78%

effective at the termination of the existing coal contract on June 30, 2022. Prior to taking over ownership from the exiting owners on June 30, 2022, Enchant, who acquired Farmington's acquisition rights in August 2019, will manage the CO_2 capture retrofit process by virtue of the Agency Agreement with the City of Farmington. The ASJPA also provides Farmington and its agent, Enchant, the right to access the site immediately for purposes of completing this FEED study.

Work on this FEED study will produce detailed engineering designs, costing, and timelines for the construction. It will also designate permitting agencies and timelines in order to execute the follow-on build and operate project. Lessons learned during the FEED study will be documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

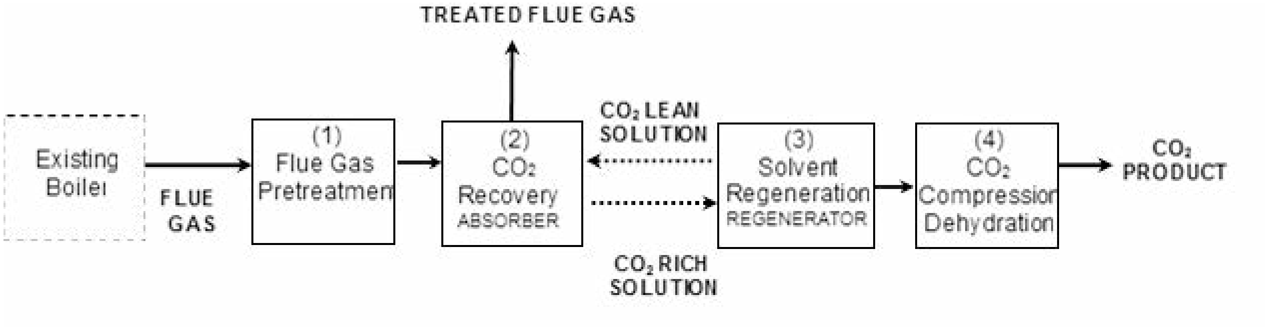

Figure 1: Block flow diagram of the CO_2 recovery plant.

The KM CDR Process has the following key features: (1) demonstrated performance on a large-scale (240 MWe); (2) high-performing amine solvent KS-1™ (high absorption capacity, low steam consumption, high resistance to oxidation and thermal degradation); and (3) key process technologies, such as an amine emission reduction system, solvent degradation reduction, automatic load adjustment control system, and amine purification system.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of SO_2 in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

In solvent regeneration, cool-rich solvent is heated by the hot-lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines.

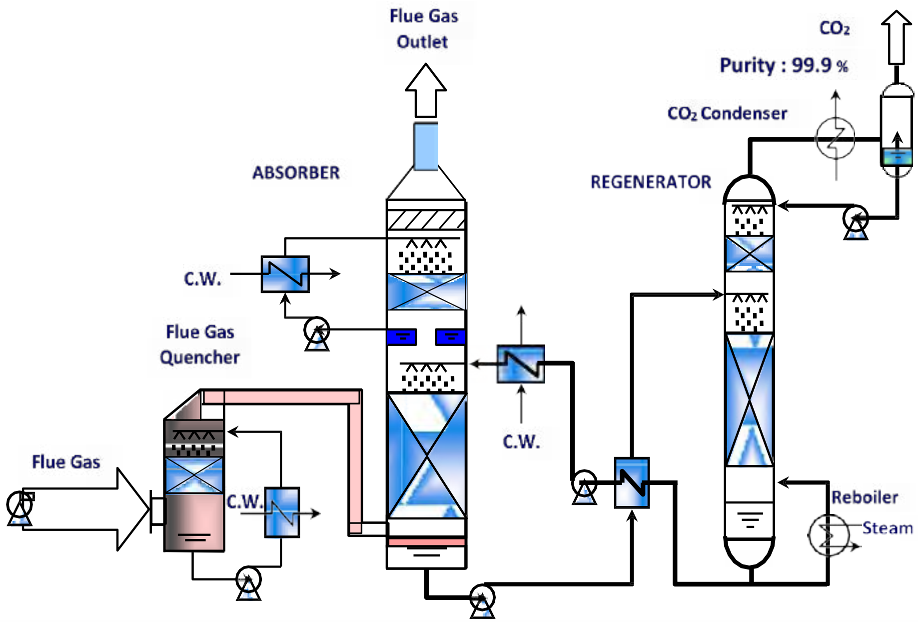

Figure 2: Carbon capture basic process flow diagram.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	proprietary data
Normal Boiling Point	°C	proprietary data
Normal Freezing Point	°C	proprietary data
Vapor Pressure @ 15°C	bar	proprietary data
Manufacturing Cost for Solvent	$/kg	proprietary data
Working Solution		
Concentration	kg/kg	proprietary data
Specific Gravity (15°C/15°C)	-	proprietary data
Specific Heat Capacity @ STP	kJ/kg-K	proprietary data
Viscosity @ STP	cP	proprietary data
Absorption		
Pressure	bar	proprietary data
Temperature	°C	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data
Heat of Absorption	kJ/mol CO_2	proprietary data
Solution Viscosity	cP	proprietary data
Desorption		
Pressure	bar	proprietary data
Temperature	°C	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data
Heat of Desorption	kJ/mol CO_2	proprietary data
Module Design		
Flue Gas Flowrate	kg/hr	5,650,894
CO_2 Recovery, Purity, and Pressure	%/ %/ barg	95% / >95 mol% dry* / 193[†]
Absorber Pressure Drop	bar	proprietary data

Estimated Absorber/Stripper Cost of Manufacturing and Installation	$ / kg/hr	proprietary data

* Pipeline requirement.

† Facility fence-line pressure requirement, downstream of CO_2 pumps.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – Estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) used in the FEED study design basis should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
11.97	127	9.93	17.16	66.91	5.98	—	19.2	106

Chemical/Physical Solvent Mechanism – Chemical absorption

Solvent Contaminant Resistance – Low solvent degradation.

Solvent Foaming Tendency – Ordinary.

Flue Gas Pretreatment Requirements – Desulfurization.

Solvent Makeup Requirements – Periodically.

Waste Streams Generated – Reclaimed waste.

Process Design Concept – Block flow/process flow diagrams shown in Figures 1 and 2.

Proposed Module Design – Partial Module Design.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Target Value ($2019) [1] (@ 85% Capacity Factor)
Total Project Cost	$	1,295,280,000
Capital Annualization Factor	--	0.1243
Annualized Capital Cost	$/yr	161,000,000
Annual O&M Cost	$/yr	99,939,000
Total Annual Cost	$/yr	260,939,000
CO_2 Captured	mmscfd	312.45
Annual CO_2 Captured	tonnes	6,000,000
Cost of Carbon Captured	$/tonne	43.49

[1] Note that target values are based on the pre-feasibility study performed prior to the DOE award (July 2019) as the project team has not finished capital and O&M cost development deliverables.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Calculations Basis – The economic calculation performed for the pre-feasibility study utilized many similar references as the Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity report Rev 2 and 3, including similar annualization factor for high-risk capital investment and 85% referenced capacity factor. Overall economics were developed using AACE Class 5 accuracy for retrofitting the existing San Juan Generating Station Units 1 and 4. For all calculation basis information, refer to the publicly available study “Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL.”

Scale of Validation of Technology Used in TEA – Costs were developed using publicly available cost information for commercially available amine-based solvent systems scaled for the size and characteristics of the SJGS facility. For information regarding capital cost development, refer to the publicly available study “Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL.”

Qualifying Information or Assumptions – Information prepared during the pre-feasibility study was not prepared in conjunction with MHI for the KM-CDR™ Process. Costing was based on 90% capture for the flue gas design basis provided in the pre-feasibility report, not herein. For all assumptions used to develop these costs, refer to the publicly available study “Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL.”

technology advantages

- FEED studies for carbon capture systems at this site will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.
- This FEED study could lead to the largest carbon capture project in the world, and with its 95% CO_2 capture rate, it could be the lowest-emitting CO_2-per-MWh large-scale, fossil-fueled power plant.
- Adding carbon capture technology will allow SJGS to meet and exceed the stringent CO_2 emissions standards of the New Mexico Energy Transition Act and will also allow for electricity sales delivered across the west, including into California under its stringent decarbonization standards.

R&D challenges

- To deploy the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large scale.

status

The design basis documents were completed, including flow diagrams, heat and material balances, equipment and instrument lists, and the preliminary plot plan. Stack testing was performed to optimize CO_2 recovery and modest design changes are expected to increase the CO_2 capture percentage from 90% warranted to the target of 95%. A hazard and operability study (HAZOP) was completed. Balance of plant planning, design, and engineering are ongoing to incorporate the CO_2 capture technology into the existing SJGS facility. Various studies and investigations are underway to provide key decisions on scope of work or selection of project-specific needs. A report of carbon production intensity was completed.

available reports/technical papers/presentations

“Preliminary Assessment of Post-Combustion Capture of Carbon Dioxide at the San Juan Generating Station: An Independent Assessment of a Pre-feasibility Study Conducted by Sargent & Lundy for Enchant Energy,”12 December 2019, Los Alamos National Laboratory. *https://www.lanl.gov/science-innovation/science-programs/applied-energy-programs/_assets/docs/preliminary-technical-assessment-december2019.pdf*.

“Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL,” July 8, 2019, Project No. 13891-001, Prepared by Sargent & Lundy. *https://www.enchantenergy.com/wp-content/uploads/2019/07/Enchant-Energy_SJGS-CO2-Pre-feasibility-Study_FINAL-Rev-0-7-8.pdf*.

“Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station,” DOE Project Kickoff Meeting, May 22, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10879&filename=Large-Scale+Commercial++Carbon+Capture+Retrofit+of+the++San+Juan+Generating+Station.pdf.*

“Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station,” 2020 NETL Project Review Meeting - CCUS Integrated Projects, August 17, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Selch.pdf*.

“Update on Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station,” 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies, August 2, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Mandelstam.pdf*.

Piperazine Advanced Stripper Front-End Engineering Design

primary project goal

The University of Texas at Austin (UT-Austin) is performing a front-end engineering design (FEED) study of the piperazine advanced stripper (PZAS) process for carbon dioxide (CO_2) capture from the natural gas combined cycle (NGCC) power plant at Golden Spread Electric Cooperative's (GSEC) Mustang Station in Denver City, Texas.

technical goals

- Develop a comprehensive estimate for the total installed cost of PZAS with CO_2 compression on an NGCC power plant.
- Provide cost details to be used in the economic optimization of the process features of PZAS and other second-generation amine scrubbing processes.
- Provide the host site and cost-share partners with the information necessary to determine whether a commercial project to capture and use CO_2 for enhanced oil recovery (EOR) can be justified.
- Provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application.

technical content

The PZAS process is a second-generation amine scrubbing process with advanced solvent regeneration for post-combustion CO_2 capture. Figure 1 shows the flow and operating conditions for PZAS as tested at the National Carbon Capture Center (NCCC) pilot plant and reflects the planned design for Mustang Station. The NGCC at Mustang Station is comprised of a combined cycle facility, which consists of two gas turbines with two heat recovery steam generators (HRSGs) and a steam turbine with a total rating of 464 megawatt-electric (MWe).

The system uses 5 molal piperazine (PZ) solvent that absorbs CO_2 two and half times faster than 30 wt% monoethanolamine (MEA), requiring only 25 feet of absorber packing height to achieve 90% CO_2 removal. Flue gas from the NGCC is contacted with PZ solvent at a lean loading of 0.20 mol CO_2/gram-equivalent PZ to remove 90% of the CO_2. The hot flue gas leaving the HRSG is cooled in the bottom section of the absorber by recirculation of rich solvent through an exchanger using air cooling, mostly eliminating the temperature bulge of the absorber. Gas leaving the middle section of the absorber is contacted with air-cooled wash water in the top section of structured packing.

Rich PZ solvent is pumped through the cold cross-exchanger, the hot cross-exchanger, and the steam heater to the sump of the stripper. A fraction of the rich solvent (5 to 10%) is heated in the cold bypass exchanger. A fraction of the warm rich solvent (20 to 40%) is bypassed at its bubble point after the cold cross-exchanger. The two bypass streams are combined and fed to the top of the stripper. The flows of the bypassed streams are optimized to minimize the steam duty. Heat is recovered from the hot lean solvent as it is returned through the hot cross-exchanger and the cold cross-exchanger and then further cooled in the trim cooler. The stripper sump is maintained at 150°C and 6.3 bar(a). Vapor from the stripper sump flows through two sections of random packing. Heat is recovered

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Piperazine Solvent with Advanced Stripper Retrofit to NGCC

participant:
University of Texas at Austin

project number:
FE0031844

predecessor project:
FE0005654

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partners:
AECOM; Trimeric Corporation

start date:
10.01.2019

percent complete:
83%

from the vapor leaving the stripper in the cold bypass exchanger. The CO_2 product is further cooled in a condenser and the water is separated and returned to the absorber water wash. The advanced stripper configuration results in a heat duty of 2.4 gigajoules (GJ)/tonne CO_2, compared to values of 2.4 to 2.7 GJ/tonne CO_2 for six other solvents tested at NCCC with the simple stripper under coal and NGCC operations. The improvement in energy performance is achieved through use of the cold rich bypass and warm rich bypass streams in the advanced stripper configuration.

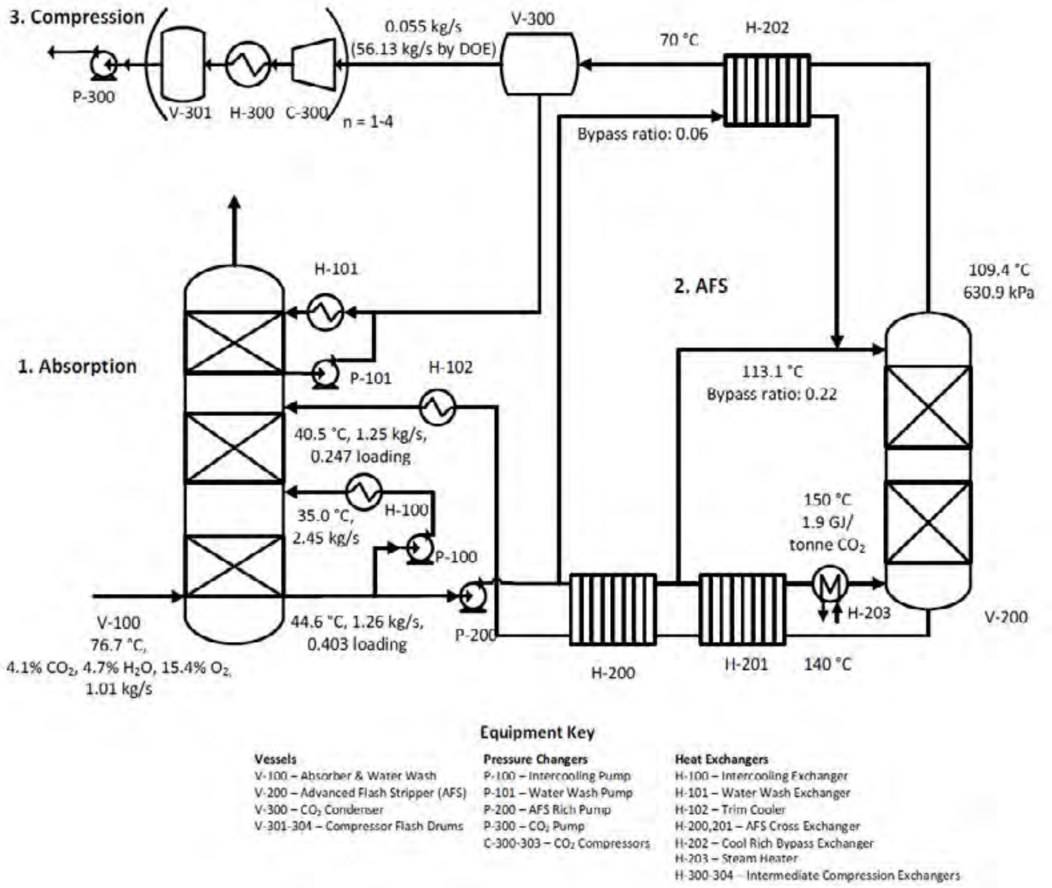

Figure 1: PZAS process flowsheet.

The PZAS process has evolved from bench-scale experiments to pilot-scale test campaigns, including testing at UT-Austin's Separations Research Program (SRP) pilot plant using simulated coal and natural gas flue gas and testing at NCCC using flue gas derived from fossil fuels at both coal and NGCC conditions. Previous testing has confirmed that PZ with a 5 molal concentration is a superior solvent to PZ with an 8 molal concentration. The reduced viscosity of 5 molal PZ results in an enhanced CO_2 absorption rate in the absorber and improved heat transfer performance in the cross-exchanger, reducing the heat duty in the advanced flash stripper (AFS) steam heater. Combining the 5 molal PZ solvent with the AFS may decrease the cost of CO_2 capture to less than $40/tonne.

The details of the techno-economic analysis (TEA) that was prepared for the PZAS process in the previous DOE-funded project DE-FE0005654 are being utilized to determine equipment sizes and to develop an approximate capital cost estimate for installing PZAS at Mustang Station. The PZAS process is estimated to require a capital investment roughly two-thirds that of other second-generation amine scrubbing processes, which is largely attributable to a significant decrease in absorber column size and modest decrease in stripper column size.

The FEED study will allow the project team to develop detailed estimates for these direct capital cost components and provide a more accurate estimate of total plant costs for a PZAS installation at Mustang Station. The resulting estimates can be used to arrive at a more accurate Lang factor for developing future cost estimates for carbon capture on NGCC plants. The project team will interface directly with vendors to obtain detailed design and cost estimates for individual pieces of equipment for a full-scale capture facility. Operating costs can be estimated based on PZAS experience at the NCCC pilot plant and the resulting TEA. Parasitic loads are calculated based on developed thermodynamic properties of PZAS and the design of heat exchangers and other equipment requiring either electricity or steam energy. An appropriate source of steam will be identified that results in maximum efficiency. The FEED will also examine the benefits and economics of integrating CO_2 captured from a power station directly into an existing CO_2 pipeline network and possibly direct use by local CO_2-EOR end-users in the area.

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

Molal Concentration (Molality) – The amount (in moles) of solute, divided by the mass (in kilograms) of the solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction of PZ with CO_2 involves formation of the following four PZ species:

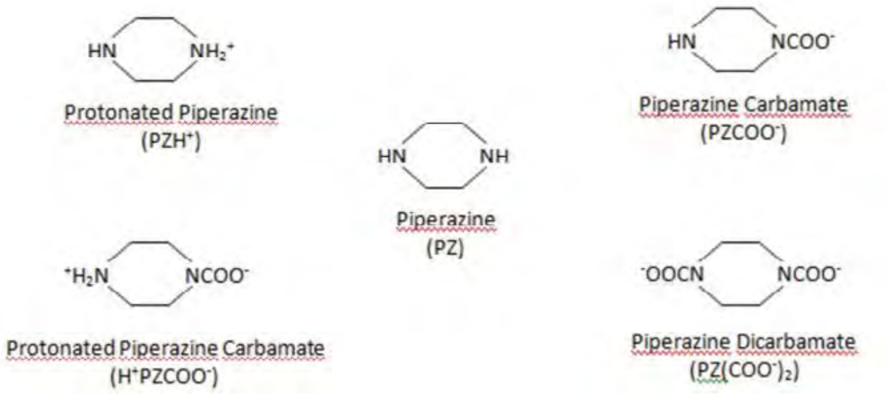

Figure 2: Molecular structure of piperazine species.

These reactions are as follows:

1. $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
2. $PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
3. $H_2O + H^+PZCOO^- \leftrightarrow H_3O^+ + PZCOO^-$
4. $PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

TABLE 1: EQUILIBRIUM CONSTANTS FOR ABOVE REACTIONS

Eq. No	Equilibrium Constant	ln K = A + B/T + C lnT		
		A	B	C
1	$K_1 = \frac{x_{PZ}x_{H3O+}}{x_{H2O}x_{PZH+}}$	-11.91	-4,351	–
2	$K_2 = \frac{x_{H3O+}x_{PZCOO-}}{x_{PZ}x_{CO2}x_{H2O}}$	-29.31	5,615	–
3	$K_3 = \frac{x_{H3O+}x_{PZCOO-}}{x_{H+PZCOO-}x_{H2O}}$	-8.21	-5,286	–
4	$K_4 = \frac{x_{H3O+}x_{PZ(COO-)2}}{x_{PZCOO-}x_{CO2}x_{H2O}}$	-30.78	5,615	–

This speciation and solubility model has been used to predict the partial pressure of CO_2 and mole fraction of species in solution as a function of PZ loading; the results show a good match between the model and the experimental data.

Solvent Contaminant Resistance – 5 molal PZ is thermally stable at 150°C with negligible oxidative (Freeman, 2011) degradation. The total amine loss is estimated to be 0.5% per week when stripping at 150°C. At 135°C, the estimated total amine loss of PZ is 0.3%, as compared to 3.0% in the case of an MEA solvent. PZ forms nitrosamines and other nitro products with nitrogen dioxide (NO_2). Both pilot-scale flue gas testing and bench-scale testing have confirmed that nitrosamines decompose at temperatures of 150°C and greater. The main degradation products of PZ are formate (0.04 mM/hr) and ammonia (0.09 mM/hr) (Freeman, 2011).

Solvent Foaming Tendency – Pilot plant tests of PZ with two different sources of coal-fired flue gas and with air/CO_2 have experienced no persistent problems with foaming. However, bench-scale experiments have shown the possibility for PZ to foam under certain conditions (e.g., after undergoing oxidation degradation). In the bench-scale tests, foaming of PZ was greatly reduced with use of an oxidation inhibitor or with use of 1 part per million (ppm) of silicone antifoam (Chen, 2011).

Solvent Makeup Requirements – Including an estimate for additional amine lost in the reclaiming process, the required makeup rate is estimated to be 0.76 kg of 30 wt% PZ per metric ton of CO_2 captured for PZ regenerated at 150°C. The estimated makeup rate for 30 wt% MEA at 120°C is approximately 2.0 kg/MT CO_2.

Waste Streams Generated – The major amine solid/liquid waste streams come from reclaimer waste. There could be fugitive liquid amine emissions, which can be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Due to the low fly ash concentration of natural gas combustion gas, the heavy metal concentration in the solvent is not expected to trigger a hazardous waste classification with this technology. Gas-phase amine emissions from the absorber can be minimized by controlling aerosol formation and aerosol emissions from the absorber. Although amine aerosol emissions, which require sulfur trioxide (SO_3) or other sources of aerosol nuclei, are not expected to be problematic with natural gas combustion, careful measurement of PZ emissions from the NCCC pilot plant with NGCC conditions have established that the PZAS process will produce less than 1 ppm PZ in the clean flue gas.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

technology advantages

As compared to conventional amine solvents, the advantages of PZ are:

- Faster CO_2 absorption rate, higher working capacity, higher thermal stability, and less oxidative degradation—all of which point toward 10 to 20% less energy use.
- Advanced stripper configuration minimizes steam heater heat duty required for regeneration, limiting equipment sizes for major process equipment.
- Elevated regeneration pressure allows for elimination of lean solvent pump and elimination of two initial stages of CO_2 compression, resulting in capital cost savings.
- High absorption rate leads to smaller absorber size, reducing capital cost.
- PZ is resistant to oxidative degradation in the absorber.
- Five molal PZ is less corrosive than MEA at typical absorber temperatures, allowing less expensive and more readily available materials of construction to be used.
- No direct contact cooler or inlet booster fan are required.

R&D challenges

- Like other amines, PZ may absorb on aerosols in flue gas, leading to high amine emissions. Aerosol formation needs to be managed.
- PZ reacts with dissolved or entrained oxygen (O_2) at temperatures exceeding 150°C, potentially leading to greater than expected solvent makeup, but still less than MEA.
- PZ forms as a solid phase with water ($PZ \cdot 6H_2O$) and also with CO_2 ($H^+PZCOO^- \cdot H_2O$). Process robustness to excursions in CO_2 loading, temperature, and water balance is being demonstrated by quantifying their effects on solids precipitation and plant operation.

status

The design basis report, hazard and operability (HAZOP) report, equipment list, and process design package have been completed. A review of the 3D model of the plant was presented to the National Energy Technology Laboratory (NETL) in October 2021. The process modeling topical report and the capital cost estimate (CAPEX) for the total installed cost of the carbon capture and compression process are nearing completion. Work continues on an economic analysis with various scenarios and improvement studies for potential major cost reductions. The final FEED report will be completed in March 2022.

available reports/technical papers/presentations

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Front-End Engineering and Design: Project Tundra Carbon Capture System

primary project goal

Minnkota Power Cooperative is performing a front-end engineering and design (FEED) study to install a post-combustion carbon dioxide (CO_2) capture system at Square Butte Electric Cooperative's Milton R. Young Station, Unit 2 (MRY2), located near Center, North Dakota. Based on the results of pre-FEED studies of two leading commercial-ready carbon capture technologies, Fluor's Econamine FG Plus^{SM} (EFG+) technology has been selected for installation.

technical goals

- Complete a FEED study for constructing the carbon capture system at MRY2, including balance of plant (BOP).
- Address final challenges to implementing CO_2 capture with studies to optimize plant efficiency.
- Finalize a permitting strategy for the overall project.
- Evaluate environmental, health, and safety (EH&S) concerns and mitigation approaches.
- Conduct a hazard and operability (HAZOP) review.
- Complete a FEED-level cost estimate and construction schedule.

technical content

Minnkota is executing a FEED study on the addition of Fluor's EFG+ technology to an existing power plant fueled by North Dakota lignite to deliver the engineering and design work needed to demonstrate the feasibility of a next-generation carbon capture system technology at world-scale. The FEED comprises a broader effort led by Minnkota, titled Project Tundra, which is an initiative to build the world's largest carbon capture facility in North Dakota and to implement carbon capture, utilization, and storage (CCUS) to preserve the use of lignite, support the CO_2 enhanced oil recovery (EOR) industry, and revitalize legacy oil fields.

The project team aims to substantiate the economics and engineering supporting the business case for construction and operation of Fluor's EFG+ technology to capture 90% (11,000 tonnes/day) of the CO_2 from the flue gas of the 477-megawatt-electric (MWe) MRY2, producing near "zero carbon" power with limited or no impact on the price of electricity.

Fluor's EFG+ technology is an advanced amine-based process tailored for removal of CO_2 from low-pressure, high-oxygen-containing flue gas (up to 15 vol%) and is used in more than 30 commercial plants worldwide to process flue gases derived from a variety of fuels. The basic plant configuration consists of a two-stage direct contact cooler (DCC) for flue gas cooling and sulfur dioxide (SO_2) removal, an absorber, a regenerator, and a compression and dehydration system to generate pipeline-ready CO_2, as shown in Figure 1. As the conditioned flue gas flows up the absorber, CO_2 is chemically absorbed into a circulating solvent stream flowing down the column. The CO_2-loaded solvent is then pumped from the bottom of the absorber, through a heat recovery exchanger where it is heated against hot

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Econamine FG Plus Retrofit to Coal-Fired Power Plant

participant:

Minnkota Power Cooperative Inc.

project number:

FE0031845

predecessor project:

N/A

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partners:

Fluor Enterprises Inc.; Burns & McDonnell; David Greeson Consulting; Hunt International Energy Services; ND Industrial Commission; EERC; Golder Associates; AECOM; Square Butte Electric Cooperative

start date:

10.01.2019

percent complete:

80%

CO_2-lean solvent, and into the top of the regenerator. As the solvent flows down the regenerator, it is contacted by steam, which strips the CO_2 from the solvent, producing an overhead mixture of steam and CO_2. The steam/CO_2 product is cooled, and the steam is condensed and separated from the CO_2 product. Hot CO_2-lean solvent from the bottom of the regenerator is pumped back through the heat recovery exchanger where it is cooled against the cold CO_2-loaded solvent before being returned to the top of the absorber.

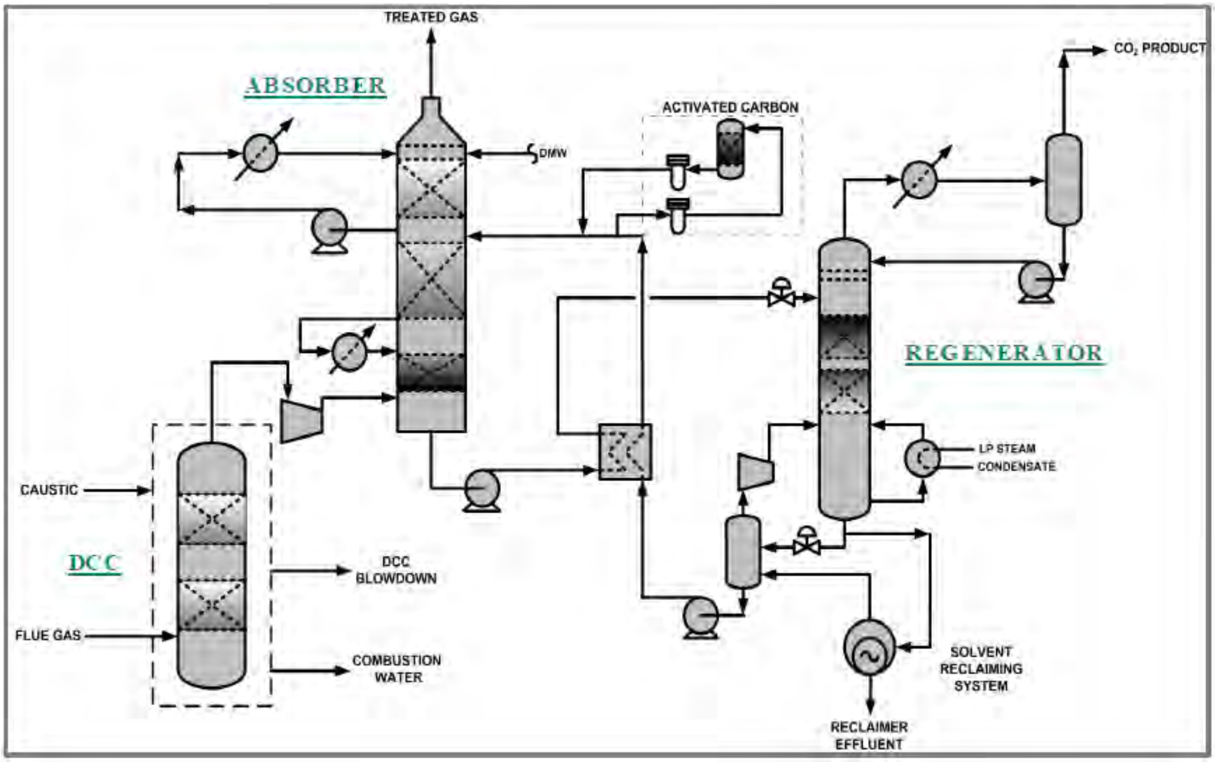

Figure 1: Schematic of Fluor's EFG+ CO_2 capture technology.

Advancements to progress the technology beyond the current state-of-the-art include steam cycle integration with advanced heat recovery to improve energy efficiency; methods for removing aerosols and a unique solvent maintenance system to minimize solvent degradation, thereby improving the environmental and cost profile; design of the world's largest capture facility (3.6 million tonnes/year, a twofold increase over any other facility) to capture greater economies of scale; optimization for cold climate performance; and establishment of the lowest levelized cost of capture attempted at world-scale.

Experience gained from Fluor's EFG+ demonstration plant in Wilhelmshaven, Germany, that captures 70 tonnes of CO_2 per day from a coal-fired power plant has enabled Fluor to make significant improvements to the process. Some of the unique features of the process design include:

- The EFG+ solvent is a proprietary formulation of primary amines with a regeneration steam requirement 30% lower than monoethanolamine (MEA).
- Fluor's patented two-stage DCC treats the flue gas in two sections, cooling the flue gas to harvest quality combustion knock-out water and removing SO_2 to single-digit part per million (ppm) levels.
- Fluor's patented absorber intercooling technology removes heat of absorption to increase the CO_2 carrying capacity of the solvent, reducing the net steam demand of the EFG+ process by 3–5%.
- A lean solvent flash/vapor compression configuration, in which the lean vapor compressor (LVC) recycles residual heat from the hot-lean solvent leaving the regenerator and transfers it back to the regenerator, resulting in a lower steam demand for the reboiler and reducing the total solvent regeneration energy requirement by approximately 10–15%.
- Minimized pressure drop in absorber due to advanced design of internals and packing in the DCC and absorber, thereby reducing the blower power by approximately 65% compared to conventional carbon capture plants.
- A solvent maintenance system (SMS) to remove heat-stable salts (HSSs) and other non-volatile degradation products in order to maintain solvent hygiene and performance.

Prior successful installations of the EFG+ process at a variety of facilities worldwide has prepared the project team for addressing new challenges, including processing a higher flue gas volume, effects from cold climate, and aerosols/solvent degradation concerns with using lignite coal-based flue gas.

The project team previously conducted a pre-FEED study to determine constructability, tie-in locations, preliminary pipe routings and interfaces, electrical interconnections, equipment specifications, capture system power requirements, geotechnical details, and control design. These components form the basis of the full FEED study, which will result in the following multidisciplinary design package:

- A FEED study report along with an electronic 3D model in SmartPlant® 3D.
- Material takeoffs (MTOs) exported from the 3D model for large-bore pipe lengths, fittings, flanges, valves, raceway, cables, and instrumentation; structural steel and concrete takeoffs developed from structural design software and sketches.
- An optimized general arrangement drawing.
- A tie-in list and location plan, with input from construction specialists during the detailed design phase; updates to process and instrumentation diagrams (P&IDs) with tie-in information.
- Detailed specifications for the major equipment packages.
- A Level 2 Process Hazard Analysis (i.e., HAZOP) report utilizing the overall P&IDs.
- A steam supply design.
- A fire protection study in accordance with National Fire Protection Agency codes and standards.
- An instrument control list with inputs and outputs and distributed control system (DCS) points, including cost specifications for all major instrument and control packages.
- Exploratory excavation plans and specifications to verify that proposed foundation and subsurface facilities are clear of obstructions.
- Preliminary foundation sketches to support equipment and ancillaries required for FEED cost estimates.
- Preliminary architectural drawings and sketches to support a cost specification for pre-engineered buildings and heating, ventilation, and air conditioning (HVAC), and obtaining budgetary quotes to support the FEED cost estimate.

Based on the pre-FEED study, a \$50/tonne 45Q tax credit for CO_2 storage or a \$35/tonne 45Q tax credit for EOR, plus projected CO_2 sales to oil companies for EOR operations, provides enough revenue to cover the capital, return on capital, and plant's operating costs, while yielding a near 10% return to tax equity. In addition, the cost of capture is expected to be \$49/tonne CO_2, which is a 20% reduction from the cost of CO_2 capture at the Petra Nova facility, the U.S.'s first commercial post-combustion carbon capture system at a coal-fired power plant. The FEED study is the next step in verifying and optimizing these costs and projections to reflect the higher level of engineering and design and cost-estimating certainty.

For the BOP items, operating cost estimates will be developed through detailed studies involving Fluor, owner's engineer Burns & McDonnell, and Minnkota. Both the operating and capital costs for an EFG+ plant are dependent on a number of variables, including, but not limited to, plant location, site conditions, plant capacity, final configuration, modularization versus field erected, flue gas conditions, air versus water cooling, and cost of utilities such as steam and electricity.

Although the EFG+ technology and the chemistry of the process are the same regardless of scale, the process equipment in the EFG+ process must be designed to ensure that the EFG+ chemistry occurs efficiently. Specifically, the scale-up challenge is construction of large-diameter columns and achieving good gas/liquid distribution in the packing.

As part of the pre-FEED, the team evaluated natural gas-fired auxiliary boiler and steam turbine extraction scenarios. Early stages of the FEED study will choose which steam source will be utilized.

In addition to removing approximately 3.6 million tonnes per year of CO_2, the carbon capture facility installed at MRY2 will also be designed to remove approximately 2,200 tonnes of SO_2 annually. However, significant concentrations of alkali-derived aerosols have been measured at MRY2 during previous studies, which can impact both amine solvent emissions and degradation rates. Also, solvent emissions from the absorber may include ppm levels of amine and degradation byproducts in the form of ammonia and aldehydes. The combination of the aldehydes/amine may constitute a new major source of VOCs, which requires a Title V permit under the Clean Air Act. In the FEED, Fluor will evaluate the cost-effectiveness of solutions for removal of aerosols upstream of the absorber, thereby eliminating/mitigating the challenge of aerosol-exacerbated emissions of amine from the absorber. Preliminary air dispersion modeling was performed in the pre-FEED study to determine appropriate stack height, parameters, and location. In order to confirm that the site will not exceed National Ambient Air Quality Standards (NAAQS), an additional air dispersion model will be required using the final FEED study parameters, emissions, and layout.

An SMS will also be included in the EFG+ plant design for MRY2 to maintain favorable solvent purity and produce a small waste effluent stream that is collected and periodically hauled offsite for disposal. Furthermore, by maintaining low impurity levels in the solvent, undesired VOC emissions are reduced dramatically.

Wastewater produced by the EFG+ plant includes blowdown from the DCC (knock-out water and SO_2 scrubbing solution). The condensed water vapor from cooled flue gas is of high quality and can be used as cooling water makeup at MRY2 after minor treatment. After investigating the compatibility of existing MRY Station wastewater treatment, Minnkota concluded that disposal via a Class I injection well is the likely method of disposal for some of the effluents. The FEED study will include design and costing of a Class I well. The proposed changes will require the MRY2 plant to modify its National Pollutant Discharge Elimination System (NPDES) permit for industrial wastewater discharges.

Any plant constructed in North Dakota requires a winterization plan, as temperatures can reach to -40°C or less. Through the pre-FEED effort, the project team identified best practices for ensuring the plant remains efficient and operational during the winter months, including specifications for building foundation depth, insulation and material specifications, cold process startup/shutdown, and buried fluid lines.

Modularization is a key component of the construction strategy for Project Tundra, which includes a transportation study to determine module size and onsite fabrication requirements. A construction-driven strategy is key to schedule certainty, risk reduction, and cost-effective execution and delivery of the project.

Flue Gas Assumptions – Unless noted, average flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
13.5	141	10.2	20.5	65.1	6.9	0.80	42.7	148.3

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is a chemical reaction.

Solvent Contaminant Resistance – The solvent has very good resistance to contaminants in the flue gas aided by the solvent maintenance system.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – SO_2 removal and temperature control is required prior to the absorber.

Solvent Makeup Requirements – Estimated at 0.25 kg/tonne.

Waste Streams Generated – Solvent maintenance system waste, water treatment waste, and cooling tower blowdown.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Proposed Module Design – Will be determined based on results of a logistics/route study.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Design Value
Cost of Carbon Captured	$/tonne CO_2	$16.60
Cost of Carbon Avoided	$/tonne CO_2	$16.60
Capital Expenditures	$/MW	$20.54
Operating Expenditures	$/MWhr	$22.58
Cost of Electricity	$/MWhr	$36.60

Definitions:

Data used:

- Average annual operating expenses (OPEX) for carbon capture system = $16.89/tonne (2025 dollars).
- Average annual CO_2 captured and avoided = 4,071,000 tonnes.
- Capital expenses (CAPEX) to place the capture system into service = $1.488 billion.
- MWe of treated flue gas = 486.5 MWe.
- Total OPEX over 20-year life of project = $1.636 billion.
- Host power plant trailing three-year average (2019–2021) cost of electricity (operations, maintenance, and fuel) = $35.6/MWh.

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – For this FEED study, the data are based on a specific plant – Minnkota Power Cooperative Milton R. Young Station.

Scale of Validation of Technology Used in TEA – While a formal TEA has not been completed, the economics are based on a full FEED study of a 486.5 MWe sized capture system, which is a scale up from the pilot scale tests at Technology Centre Mongstad.

Qualifying Information or Assumptions:

- Dollar values include escalation at 2%.
- Annual combined (host + carbon capture and storage [CCS]) capacity factor = 85%.
- All costs and production estimates are based on CO_2 delivered to the fence line of the CCS dehydrated and compressed to 1,500 pounds per square inch (psi) (i.e., “pipeline quality” ready for shipment).
- Transport and storage of CO_2 is not included in these numbers.

technology advantages

- Advanced solvent formulation with high CO_2 capacity and high absorption rate.
- Low pressure-drop packing in DCC and absorber has the potential to lower the power consumption for the blower by 65%.
- Large diameter column design for absorber and DCC reduces the number of absorption trains required, thereby lowering capital costs.
- Novel absorber intercooler configuration increases solvent loading and lowers the overall solvent circulation rate, further reducing power consumption and solvent loss.
- An LVC unit reduces the steam demand for solvent regeneration by 10–15%.
- Fluor’s proprietary SMS lowers overall solvent loss and makeup.
- Advanced reclaiming technology significantly reduces reclaimer waste.

R&D challenges

- Lignite coal-based flue gases, such as that produced at MRY2, contain alkali-derived aerosols and particulate matter that can have a detrimental impact on both amine solvent emissions and degradation rates.
- Integration into an existing facility poses many operating and plant layout challenges.

- Maintaining a proper water balance for the facility becomes a challenge.

status

The project team developed an optimized design manual of the carbon capture system, including analyses for integrating the carbon capture system with the plant's steam cycle or utilizing natural gas-fired auxiliary boilers. The gas-fired boilers were selected as the basis for the FEED study. The capture facility was increased in size to accommodate the flue gas from the gas-fired boilers, resulting in the ability to remove approximately 4.0 million tonnes of CO_2 versus the pre-FEED levels of 3.6. The boilers also allowed for additional flexibility in the operation by allowing a tie to the MRY1 unit flue gas duct for operation when MRY2 is offline. Design and integration of the carbon capture system with BOP was completed and a HAZOP review was conducted. Meetings were held with the North Dakota Department of Environmental Quality to discuss the requirements for air emissions and water discharge permitting. An initial permitting strategy was finalized to comply with air, water, and waste product regulations that will support permit applications. Project Tundra cost estimating has been completed, including preparation of a FEED-quality estimate, as well as a schedule for the engineering, procurement, and construction phases of the project. Initial efforts resulted in higher capital cost than anticipated, so a cost reduction effort was initiated to come up with various ideas to reduce costs along with rough estimates. One of the major cost increases was due to refinement of the gas-fired boiler capital and fuel costs. Preliminary efforts were initiated to look at the steam extraction in more detail.

A final report is being prepared, summarizing all project results and analyses and making recommendations for future research and development (R&D). Further refinement of cost-reduction ideas and steam extraction will need to take place outside the scope of this FEED study as the project proceeds.

available reports/technical papers/presentations

"Front-End Engineering & Design: Project Tundra Carbon Capture System," DOE Kickoff Meeting, November 12, 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10890&filename=Front-End+Engineering+%26+Design%3a+Project+Tundra+Carbon+Capture+System.pdf.*

"Front-End Engineering & Design: Project Tundra Carbon Capture System," presented at the 2020 NETL Project Review Meeting - CCUS Integrated Projects, August 17, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Pfau.pdf*

"Front-End Engineering & Design: Project Tundra Carbon Capture System," presented at the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies, August 2, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Pfau.pdf*

Front-End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant

primary project goal

Southern Company Services Inc. is conducting a front-end engineering design (FEED) study for a carbon dioxide (CO_2) capture system based on Linde-BASF's aqueous amine solvent-based technology installed at an existing Southern Company natural gas-fired combined cycle (NGCC) power plant. A commercial scale (at least ~375 megawatt-electric [MWe]) CO_2 capture plant is being designed to achieve a high removal of CO_2 from the flue gas feed stream.

technical goals

- Select an NGCC generating plant as the host site for the FEED study based on a set of defined criteria (performance of the gas turbines, availability of space to house a carbon capture system, availability of utilities to support the system, suitability of the surrounding geology for enhanced oil recovery [EOR] or storage).
- Produce a design basis for the carbon capture system based on the specific site requirements, including flue gas composition, environmental requirements, and requirements for modularization.
- Complete a conceptual design package for the process area of the post-combustion capture plant and assess the logistics for solvent delivery required for a commercial-scale carbon capture plant.
- Complete design packages for mechanical, electrical, structural, instrumentation and control, and facilities engineering and assess the cost and logistics for constructability and site security.
- Utilize the cost and schedule estimates of equipment vendors and contractors to derive a total project cost and schedule estimate within ±15% error.

technical content

Linde and BASF have been jointly developing, optimizing, and testing an advanced post-combustion CO_2 capture technology since 2007. The Linde-BASF technology for capturing CO_2 from flue gas using the BASF OASE® blue solvent is a mature technology that has been tested in two pilot plants with different flue gas sources, covering a wide variety of flue gas compositions and impurities. The Linde-BASF aqueous amine solvent-based post-combustion CO_2 capture technology provides a solution for key challenges encountered by solvent-based carbon capture technologies, which include relatively high capital costs, significant parasitic energy requirements, and solvent stability and degradation issues.

The technology is based on a typical lean-rich solvent absorption/regeneration cycle for CO_2 capture, but leverages several key innovative features for both

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Linde-BASF Amine Solvent-Based Technology Retrofit to NGCC Plant

participant:
Southern Company Services Inc.

project number:
FE0031847

predecessor projects:
N/A

NETL project manager:
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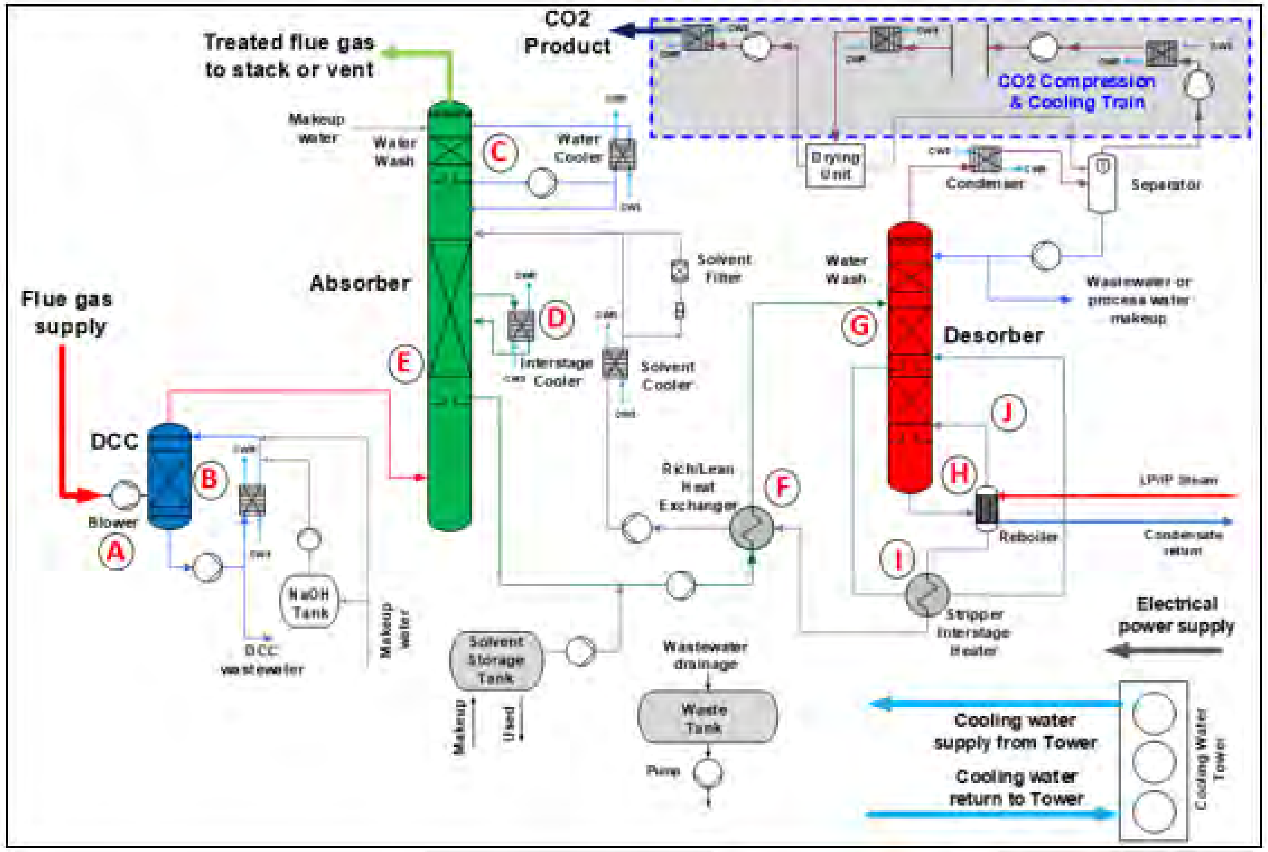
principal investigator:
Landon Lunsford
Southern Company
LDLUNSFO@southernco.com

partners:
Linde Gas North America LLC; BASF; Linde Engineering Dresden

start date:
01.29.2020

percent complete:
90%

solvent and process optimization to reduce the cost of CO_2 capture from NGCC plants. The optimized properties of the OASE blue solvent led to capital and operating cost reduction due to efficient CO_2 capture from low pressure sources through favorable reaction kinetics and reduced reboiler steam energy consumption; better stability than monoethanolamine (MEA); and a lower solvent circulation rate. In addition to advances in solvent design, Linde has achieved significant improvements in process design, as outlined in Figure 1.



A. Flue gas blower provides sufficient pressure to overcome pressure drop across the direct contact cooler (DCC)/pre-scrubber and absorber. The blower location can be adjusted to minimize cost based on arrangement of equipment and piping at the NGCC site.
B. Integrated DCC/pre-scrubber to reduce sulfur oxides (SO_X) content below 5 parts per million (ppm) and simultaneously cool the flue gas stream to ~35–40°C.
C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols. Dry bed configuration helps mitigate aerosol-driven amine losses.
D. A gravity-driven inter-stage cooler for the absorber that eliminates the need for a pump and related controls.
E. High-capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction and greatly reduced capital costs.
F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.
G. Regenerator designed for operation at pressures up to 3.4 bara significantly reduces CO_2 compression energy and eliminates the bulky first stage of the CO_2 compressor, resulting in capital cost savings.
H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to flue gas load and composition changes.
I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.
J. Variations of the stripper-reboiler flashing configuration, which are being evaluated to further minimize solvent regeneration energy.

Figure 1: Process flow diagram of Linde-BASF OASE blue post-combustion CO_2 capture technology.

A development timeline of the Linde-BASF technology is shown in Figure 2. Previous testing of a 0.45-MWe dry lignite-fired pilot plant incorporating the Linde-BASF technology has shown that the OASE blue solvent is more stable than MEA after 2,500 hours of testing. The process was also previously tested at 1.5-MWe-scale at the National Carbon Capture Center (NCCC) under the U.S. Department of Energy (DOE)-funded project DE-FE0007453, validating solvent stability and revealing a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact.

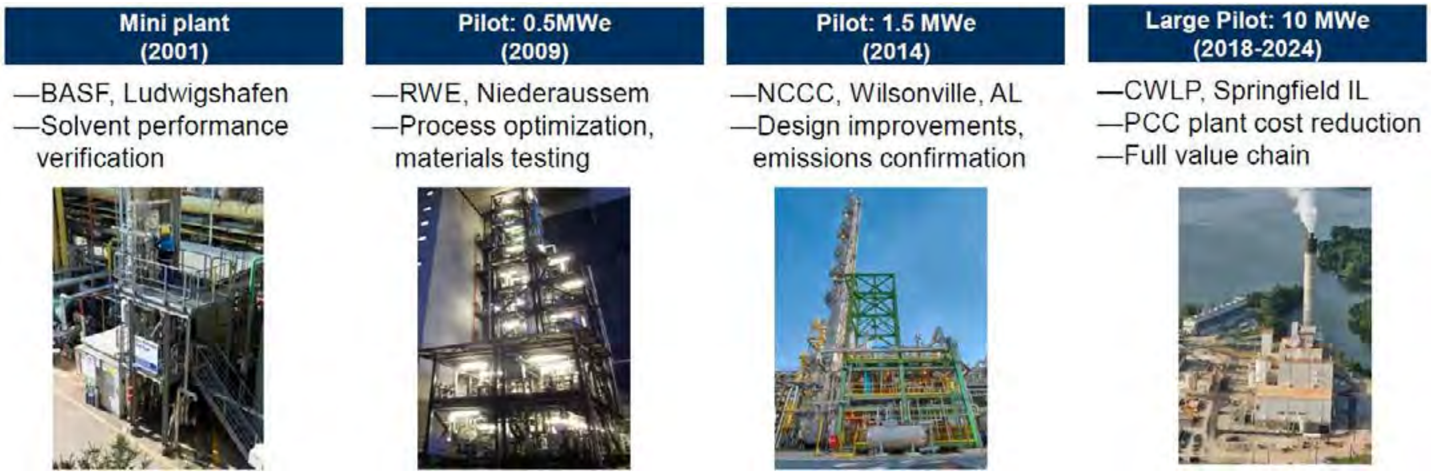


Figure 2: Linde-BASF post-combustion CO_2 capture technology development.

Milestones achieved thus far for the Linde-BASF post-combustion CO_2 capture technology applied to NGCC flue gas conditions are outlined in Figure 3. These include testing on an NGCC flue gas composition at the 0.45-MWe pilot-scale in Niederaussem, Germany; completion of a detailed FEED study on CO_2 capture from a 510-MWe NGCC power plant in 2011; and completion of a pre-FEED study for CO_2 capture at a 480-MWe NGCC power plant in 2018.

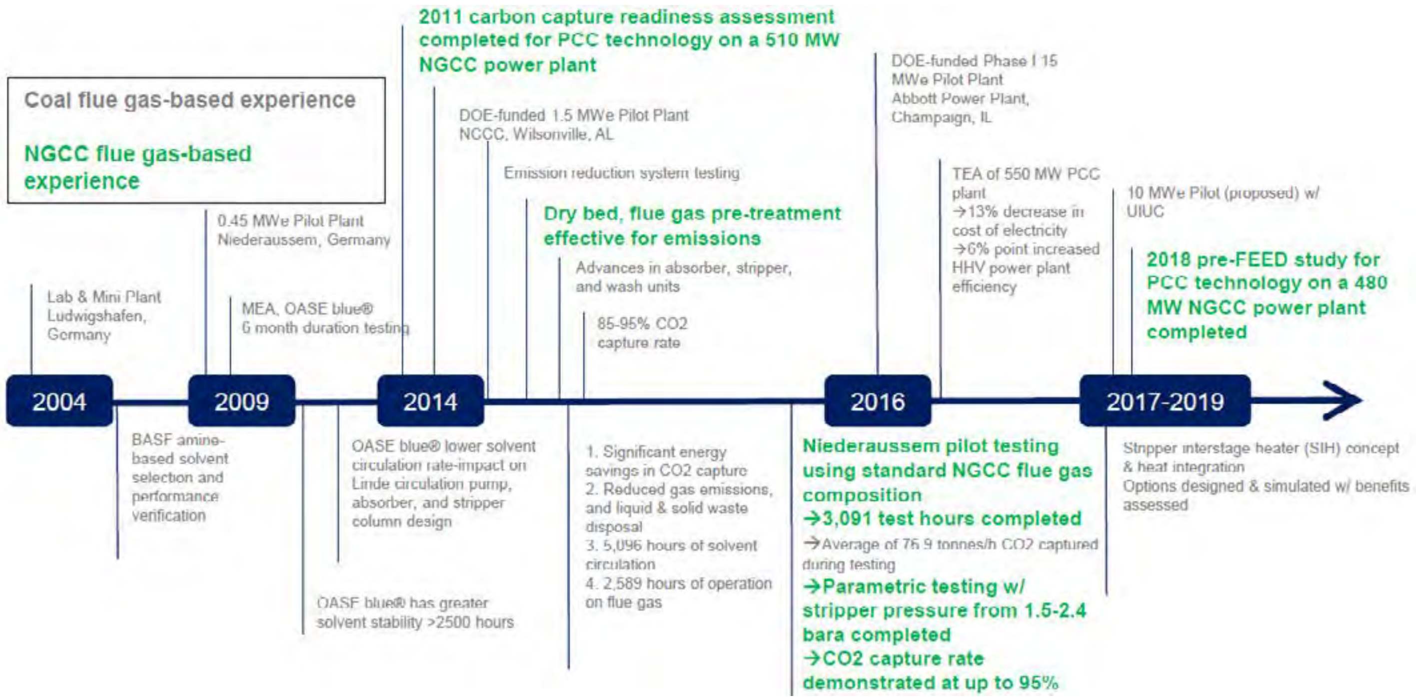
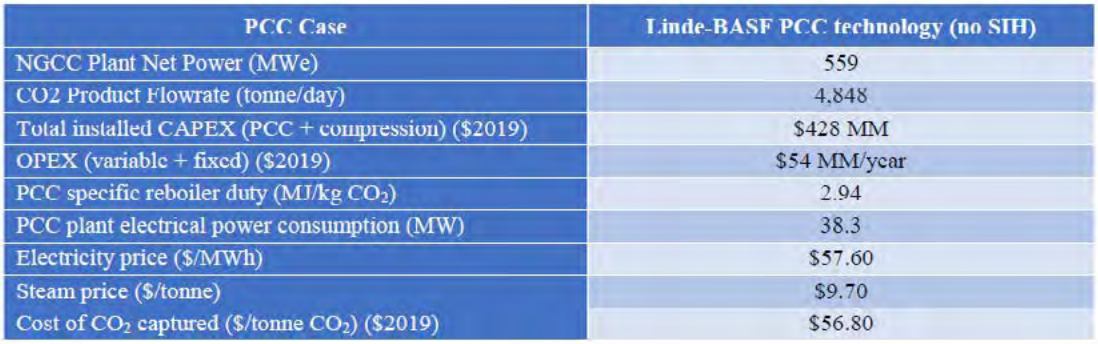


Figure 3: Milestones achieved by Linde-BASF post-combustion CO_2 capture technology.

The capital and operating costs determined from the previous pre-FEED and FEED studies are shown in Table 1. The studies were based on commercial Linde-BASF post-combustion CO_2 capture plants recovering 85–90% of the CO_2 in the flue gas supplied to the process from an NGCC power plant. All major process components were included in each study and the CO_2 product purity was specified at greater than 99 mol% (dry) with less than 100 parts per million (ppm) oxygen (O_2) content. Capital costs were estimated using Linde's proprietary cost estimation methodology for new commercial plants and were derived from databases of actual equipment quotes from vendors collected from recent projects. Capital costs for CO_2 capture plants integrated with NGCC plants are significantly higher compared to those integrated with coal-fired power plants due to the reduced flue gas CO_2 concentration in natural gas-derived flue gas (~4 mol% versus ~12% mol% CO_2 for coal-fired plants). This reduced flue gas CO_2 concentration necessitates a taller and larger diameter absorber column to achieve 90% CO_2 capture at low or ambient pressures. The optimum CO_2 capture rate at the host site will be defined in the FEED study to achieve an attractive cost option.

TABLE 1: ESTIMATED CAPEX, OPEX, AND COST OF CO_2 CAPTURED FOR LARGE-SCALE LINDE-BASF CO_2 CAPTURE AND COMPRESSION PLANT (550+ MWE) FOR NGCC BASED ON PAST LINDE STUDIES (COST YEAR=2019) (WITHOUT TRANSPORTATION AND STORAGE)



PCC Case	Linde-BASF PCC technology (no SIH)
NGCC Plant Net Power (MWe)	559
CO2 Product Flowrate (tonne/day)	4,848
Total installed CAPEX (PCC + compression) ($2019)	$428 MM
OPEX (variable + fixed) ($2019)	$54 MM/year
PCC specific reboiler duty (MJ/kg CO_2)	2.94
PCC plant electrical power consumption (MW)	38.3
Electricity price ($/MWh)	$57.60
Steam price ($/tonne)	$9.70
Cost of CO_2 captured ($/tonne CO_2) ($2019)	$56.80

The general approach for the FEED follows the methodology described in Figure 4.

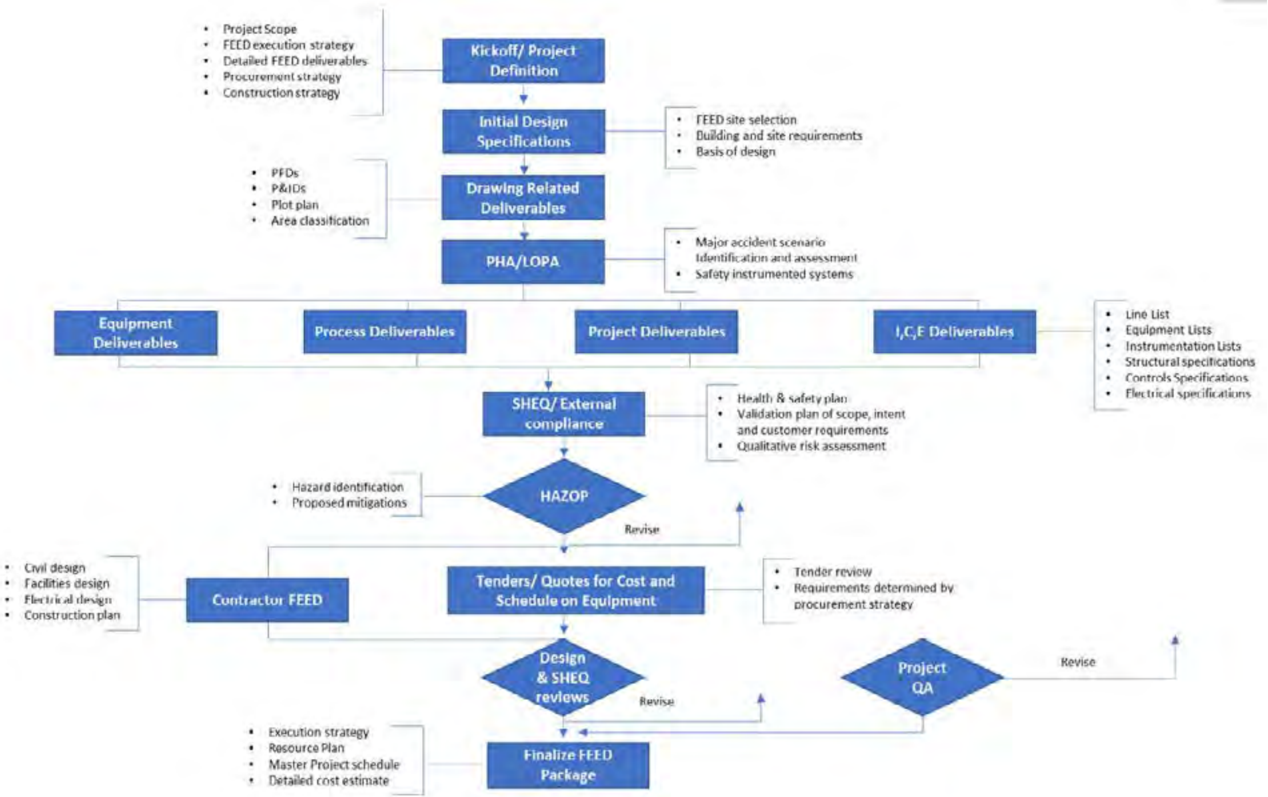


Figure 4: FEED approach.

Process designs that reduce the energy required for solvent regeneration through heat recovery integration are being optimized as part of the FEED study. Waste heat sources at the NGCC-fired host site can be leveraged to reduce the parasitic steam consumption of the CO_2 capture system and reduce the negative impact of the capture plant on power plant steam cycle efficiency or net electrical power generation. Sources include: (1) supplemental low- to medium-pressure steam from the power plant steam cycle in the range of 5–6 bara not currently used for electricity production can be redirected for use in the post-combustion CO_2 capture plant reboiler; (2) waste heat recovered from the hot flue gas upstream of the CO_2 capture plant after the heat recovery steam generator (HRSG) can be used to pre-heat CO_2-rich solvent entering the stripper column; or (3) external steam generation can reduce the steam input from the power plant. In addition, process optimization within the post-combustion CO_2 capture plant itself, including lean vapor compression (LVC) involving flashing of the CO_2-lean solution at the bottom of the stripper and redirecting the vapor after compression back to the bottom of the stripper, is an option that can substantially reduce the reboiler steam consumption for NGCC-fired CO_2 capture down to 2.4 gigajoules (GJ)/tonne CO_2 based on past FEED studies conducted for large Linde-BASF post-combustion CO_2 capture plants.

Linde has conducted extensive research on the management of flue gas aerosol particles that contribute to amine losses through the treated gas exiting the absorber, including both literature studies and aerosol measurements taken during testing of the Linde-BASF post-combustion CO_2 capture technology at NCCC. Experimentally, Linde has determined that if aerosol concentrations are less than 10^7 particles/cm^3 for particles ranging from 70–200 nanometer (nm) in diameter, there is no need for pre-treatment beyond a direct contact cooler (DCC)/pre-scrubber and dry bed wash section in the absorber to manage the aerosols. Aerosol concentrations are expected to be much lower for NGCC-derived flue gas than for coal-fired flue gas; therefore, typical emissions control measures have been integrated into the Linde-BASF CO_2 capture plant design.

Two Southern Company host sites are being evaluated in the first phase of the FEED study: Alabama Power Company's Plant Barry (Units 6 and 7), located in Bucks, Alabama, and Mississippi Power Company's Plant Daniel (Units 3 and 4), located in Moss Point, Mississippi. Each of the gas-fired combined cycle units (Units 6 and 7 at Plant Barry and Units 3 and 4 at Plant Daniel) produce a nominal 525 MWe (net). For either host site, equipment and operating modifications in the combined cycle to increase CO_2 concentration in the flue gas is a primary focus of the FEED study to minimize carbon capture costs. Cooling water capacity at both combined cycle plants is limited; therefore, evaluations of new cooling tower capacity versus air cooling are being performed in the FEED. For each site, steam supply to the carbon capture process may be available via extraction from the steam turbine, but the overall impact on the HRSG, steam cycle, and steam turbine is being evaluated during the FEED to determine the cost impact of extraction versus alternate steam production from a package boiler or cogeneration unit.

The FEED will provide a financial indicator of the costs of installation at an actual domestic NGCC power plant site and potentially illustrates that this capture system can be employed at operating commercial coal-fired power plants. The commercial FEED will provide a realistic framework for NGCC power plants to be built CO_2 capture-ready or to retrofit existing NGCC plants with an economical CO_2 capture system.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	proprietary
Normal Boiling Point	°C	proprietary
Normal Freezing Point	°C	-5 to 25
Vapor Pressure @ 15°C	bar(a)	proprietary
Manufacturing Cost for Solvent	$/kg	proprietary
Working Solution		
Concentration	kg/kg	proprietary
Specific Gravity (15°C/15°C)	-	1.0 – 1.2
Specific Heat Capacity @ STP	kJ/kg-K	proprietary
Viscosity @ STP	cP	1.5 – 7.0
Absorption		
Pressure	bar(a)	0.9 – 1.1
Temperature	°C	30 – 60
Equilibrium CO_2 Loading	mol/mol	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary
Solution Viscosity	cP	1.5 – 7
Desorption		
Pressure	bar(a)	1.6 – 3.4
Temperature	°C	125 – 140
Equilibrium CO_2 Loading	mol/mol	proprietary

Heat of Desorption	kJ/mol CO_2	proprietary
Module Design		
Flue Gas Flowrate	kg/hr	Designed for >375 MWe slipstream
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, >99.9% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	proprietary
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the HRSG unit (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**			vol%			ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.8	231	4	9	74	12	1	0.08	2

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbon dioxide in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operations, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 ppm in order to limit solvent degradation and is implemented in a DCC in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE blue solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the DCC where SO_X and nitrogen oxide (NO_X) are removed; this stream is typically handled in the power plant wastewater treatment facility. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – Flowsheet/process flow diagram shown in Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

technology advantages

- Exhibits a lower solvent circulation rate, reduced reboiler steam energy consumption compared to process using MEA solvent, reduced absorber diameter due to high efficiency packing, and lower downstream CO_2 compression cost due to the ability to operate at higher desorber pressures.
- BASF is the producer of the OASE blue solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.
- The Southern Company-Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant engineering, procurement, and construction (EPC); commercial deployment; and long-term, continuous operations.

R&D challenges

- Carryover and emissions of amines and amine degradation products.
- Handling large volumes of process condensate from DCC.
- Disposal of spent activated carbon and filters can generate solid waste management issues.
- Designing for low liquid/gas ratios caused by lower CO_2 concentration in natural gas flue gas may result in below-target CO_2 capture rate and/or vapor and liquid maldistribution.
- Equipment scale-up associated with large vapor flows due to low CO_2 concentration.
- Engineering the liquid hydraulics and gas distribution in large manifolds needed for multiple absorbers.
- Integration of post-combustion CO_2 capture plant with host site.

status

The project team selected Plant Daniel (525 MWe) in Mississippi as the host site for the FEED study employing the Linde-BASF CO_2 capture technology. The basic design and engineering reports were completed with heat and material balances, process flow diagrams, preliminary process and instrumentation diagrams, and a steam source study. The FEED study report is being finalized, including a hazard and operability (HAZOP) review and engineering documents for mechanical and piping; instrumentation, controls, and electrical; civil and structural; and facilities. An estimate of the cost and schedule is also being prepared. A final FEED package with the engineering deliverables, cost estimate, and schedule will be submitted to DOE at the end of Q1 calendar year (CY) 2022. After project completion, a final report will be prepared and submitted in Q2 CY 2022, summarizing all project results and analyses, and making recommendations for future research and development.

available reports/technical papers/presentations

Lundsford, Landon, "Front End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant," presented at the 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting - Integrated CCUS Projects and FEED Studies, August 2, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Lunsford.pdf*.

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[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Front-End Engineering Design Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Gas Turbine Combined Cycle Power Plant

primary project goal

Bechtel National, Inc. has performed a comprehensive front-end engineering design (FEED) study for a carbon capture and compression plant retrofit to an existing natural gas-fired combined cycle (NGCC) power plant located in Texas. The capture plant is based on conventional technology comprising a non-proprietary aqueous solvent, monoethanolamine (MEA), an absorber-stripper cycle, and multi-stage centrifugal compressors.

technical goals

- Developed a project design basis to provide general project requirements that apply to the specific plant site, ambient conditions, fuel feedstock and flue gas characteristics, environmental requirements, and modularization design requirements.
- Developed process engineering documents for constructing the carbon capture system, including block flow diagrams, heat and mass balance diagrams, process flow diagrams for major components, piping and instrumentation diagrams, and a water balance diagram.
- Conducted a preliminary hazard and operability (HAZOP) study and produced a report to document the results.
- Developed civil, structural, mechanical, electrical, and control systems engineering design packages.
- Developed a layout and design package that includes process plant arrangement drawings and piping and instrumentation diagrams.
- Summarized expected emissions and waste streams.
- Reviewed various contracting and purchasing options for procuring a new process system and performed a constructability review to identify construction access, lay-down areas, and sequencing of construction work.
- Developed an overall project capital cost estimate within a ±15% accuracy.
- Prepared a final FEED study package that is available for public use.

technical content

Bechtel executed a FEED study on retrofitting an existing NGCC power plant with an amine-based post-combustion carbon capture plant. The prospective end use for the captured carbon dioxide (CO_2) is enhanced oil recovery (EOR). Bechtel has developed a technology readiness level (TRL) 9 carbon capture, utilization, and storage (CCUS) concept for retrofitting an existing NGCC with mature and field-proven technology and equipment. Figure 1 illustrates a simplified process flow diagram of a conventional absorber-stripper scrubbing system with a non-proprietary solvent such as MEA.

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Amine-Based Solvent Technology Retrofit to NGCC Plant

participant:
Bechtel National, Inc.

project number:
FE0031848

predecessor projects:
N/A

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partners:
Electric Power Research Institute, Inc.; Nexant

start date:
10.01.2019

percent complete:
100%

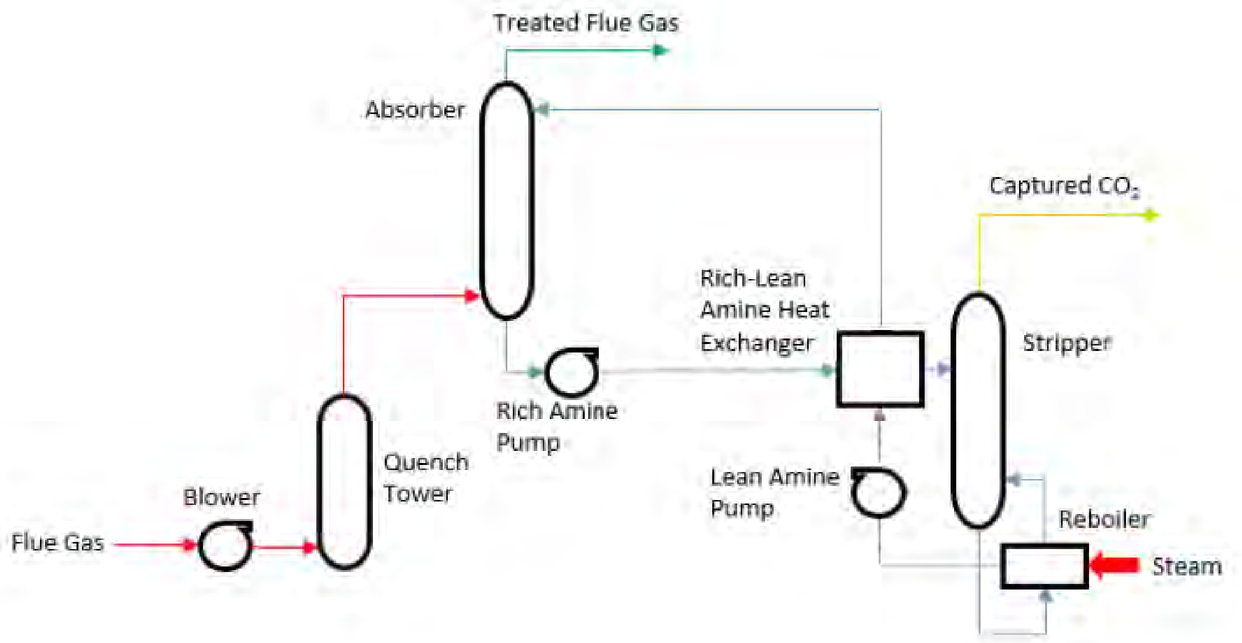

Figure 1: Generic simplified flowsheet for amine-based CO_2 capture from flue gas.

Bechtel has applied an “open access” and “open technology” methodology to the process and physical design of the facilities and the solvent used in the technology. An “open access” technology approach denotes that the owner/operators of a post-combustion carbon capture plant are in full control of the technology used in the plant. The post-combustion carbon capture hardware can be procured by competitive tendering against a non-proprietary specification, similar to conventional power plants. This allows the owner/operators to specify the post-combustion carbon capture plant hardware and solvent selection based on the latest published technology and operating experience. “Open access” technology utilizes a generic, non-proprietary solvent that is readily purchased on the open market from chemical manufacturers at a relatively low cost. These features facilitate lower capital and operating expenses and avoid royalty payments and technical restrictions associated with the use of proprietary system designs and solvent selection.

The host site selected for the FEED study is the Sherman Generating Station, a 2x2x1 NGCC located in Sherman, Texas. The 758-megawatt-electric (MWe) power plant built by Bechtel is powered by two Siemens F class gas turbines. The selection of the site has several advantages, including:

- The NGCC plant was built by Bechtel; therefore, key project personnel have access to all design documents and are familiar with the facility.
- The plant includes F class gas turbines, a state-of-the-art technology.
- The location of the host plant is near oil-bearing formations favorable for EOR operation.

Lessons learned and experience gained from earlier FEED and FEED verification studies performed by Bechtel were used as a basis for this FEED study. Bechtel prepared a FEED verification in 2015 under the direction of Shell for a proposed carbon capture retrofit to gas turbine Unit 13 at the Peterhead Power Station in Scotland. In 2009, Bechtel performed a FEED study for a CO_2 capture and compression facility designed to capture 85% of the CO_2 emissions from a 420-MWe gas-fired power plant in Norway. Both a proprietary solvent and MEA were used as bases of design. The plants involved in both FEED studies employ Siemens gas turbines, similar to the gas turbines in the Sherman facility; thus, much of the engineering work has already been completed by Bechtel for flue gas conditions very similar to the host site in Texas. Bechtel’s FEED report is based on these past design reports.

The major deliverable of this completed FEED study is a design package that includes the following topic areas: flue gas blower and quench, CO_2 absorption, semi-lean amine system, CO_2 stripping and heat integration, CO_2 compression and drying, CO_2 pumping and dense phase transfer, amine reclaiming, and amine storage. It was found in this case study that the baseline CO_2 capture cost is \$114.50/tCO_2 (when including both annualized capital and annual operations/maintenance), that the energy penalty on the powerplant is 67.3 MW, that the average forgone electricity revenue is equivalent to \$13/tCO_2 captured, and that a pilot testing program should be used to resolve design uncertainties (such as amine degradation rates).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	61.08
Normal Boiling Point	°C	170
Normal Freezing Point	°C	10.3
Vapor Pressure @ 15°C	bar	<1
Manufacturing Cost for Solvent	\$/kg	1 – 2
Working Solution		
Concentration	kg/kg	35
Specific Gravity (15°C/15°C)	—	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.6
Viscosity @ STP	cP	4
Absorption		
Pressure	bar	1.089
Temperature	°C	53.5
Equilibrium CO_2 Loading	mol/mol	0.4 – 0.49
Heat of Absorption	kJ/mol CO_2	TBD
Solution Viscosity	cP	2.56
Desorption		
Pressure	bar	2.31
Temperature	°C	130.8
Equilibrium CO_2 Loading	mol/mol	0.22 – 0.25
Heat of Desorption	kJ/mol CO_2	TBD
Module Design		
Flue Gas Flowrate	kg/hr	2.53×10^6
CO_2 Recovery, Purity, and Pressure	% / % / bar	80-90 / 99.0+ / 200
Absorber Pressure Drop	bar	0.076
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	TBD

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.038 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical natural gas fired combined cycle power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 3.82 %. Therefore, the partial pressure of CO_2 is roughly 0.0382 atm or 0.0387 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the heat recovery steam generator (HRSG) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	194	3.82	7.74	74.78	12.81	0.85	-	2

Parameter Descriptions:

Flue Gas Pretreatment Requirements – Flue gas is cooled to approximately 50°C before entering absorber towers through a fogging system that reduces temperature and saturates flue gas with water.

Solvent Makeup Requirements – Detailed in the FEED report.

Chemical/Physical Solvent Mechanism – The chemical/physical solvent mechanism is primarily controlled by the solubility and alkalinity characteristics of the amine. MEA is fully water soluble and exhibits high alkalinity. MEA's low molecular weight permits higher solution capacity and its low boiling point allows higher recovery during reclamation of contaminated solution. Carbon dioxide solubility in MEA solutions is relatively high. Regeneration of MEA solutions is accomplished at reasonable temperatures with moderate heat input. Further discussion is included in the FEED report.

Solvent Contaminant Resistance – Detailed in the FEED report.

Solvent Foaming Tendency – Detailed in the FEED report.

Waste Streams Generated – MEA and ammonia emissions from the absorber are reasonable and are defined in the FEED report. Liquid and solid wastes from solvent maintenance and reclaiming is defined in the FEED report.

Process Design Concept – The process overview under normal operation consists of the following systems:

- Flue gas diversion—The flue gas is directed from the existing stack to the plant.
- Flue gas cooling—The flue gas as supplied is too hot to process efficiently in the absorber and is cooled to its saturation temperature before entering the absorber.
- CO_2 absorption—Parallel absorbers use an amine solution to remove the CO_2 from the flue gas.
- Heat integration—Heat is recovered from internal streams to enhance plant energy efficiency.
- CO_2 stripping—The amine is regenerated for reuse by liberating the CO_2 from the amine solution.
- CO_2 compression and drying—The CO_2 is compressed, dried, further compressed, and liquefied to meet the CO_2 specifications.
- Amine reclamation—Heat stable salts (HSS) and degradation/oxidation products are removed from the amine solution.
- Amine storage—Fresh amine and lean amine are stored and injected into the absorption system to maintain the amine solution concentration.

Proposed Module Design – Detailed in the FEED report.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	114.50	114.50
Cost of Carbon Avoided	\$/tonne CO_2	136.50	136.50
Capital Expenditures	\$/MWhr	32.43	32.43
Operating Expenditures	\$/MWhr	11.50	11.50
Cost of Electricity	\$/MWhr	63.93	63.93[1]

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions

Calculations Basis – Data are based on Panda Power's Sherman Natural Gas-Fired Combined Cycle Power Plant located in Texas.

Scale of Validation of Technology Used in TEA:

- This study used the ProMax® process simulation software to develop the mass and energy balances for the design energy case. The Carbon Capture Simulation Initiative (CCSI) Toolset (by the National Energy Technology Laboratory [NETL]) was also applied to compare results using the ASPEN Plus simulation package. Results from the two modelling tools were evaluated to identify uncertainties. Because of those modelling uncertainties, pilot plant testing was recommended before proceeding to full-scale plant design.
- Costs were based on actual costs from quotes for full-scale facility and costs for construction.
- MEA has been extensively piloted at the National Carbon Capture Center (NCCC) in Alabama and at Test Center Mongstad in Norway.

Qualifying Information or Assumptions:

- Capital cost estimate based on worldwide sourcing.
- Costs are specific to the Sherman, Texas, site.
- Estimate includes builders risk insurance and general liability.
- Operating hours per year: 5,000.
- Level of operation: 420 MW equivalent.
- Average value of reduced electricity sales to the Electric Reliability Council of Texas (ERCOT): \$25/MWhr.
- Electricity sales reduction: 67.3 MW.

technology advantages

- Use of generic solvent avoids restrictions and costs associated with proprietary solvents.
- An "open access" and "open technology" approach can accelerate CCUS deployment and reduce the costs of CCUS by facilitating efficient know-how exchange and competition within the fleet of plants that may be built over the next five to 10 years.

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[1] Assumed cost of electricity is \$20.00 per MWh without carbon capture.

- "Open access" and "open technology" full-scale plants can facilitate the progression of post-combustion capture systems currently at TRL 9 to achieve a commercial readiness index of 6 within 10 years or less.
- Bechtel has extensive experience in carbon capture studies, plus detailed design, construction, and operation of NGCC power plants and CO_2 capture plants, including involvement in several previous FEED studies on CO_2 capture retrofits to NGCC plants.

R&D challenges

- Steam extraction complexity.
- Confirmation of carbon capture simulation software accuracy for generic amine solutions at high solvent strengths.

status

The project team has developed final engineering documents that include block flow diagrams, process flow diagrams, heat and mass balances, water balance diagrams, piping and instrument diagrams, and summary equipment specifications. Engineering design packages were prepared for civil, structural, mechanical, electrical, automation, and environmental systems.

available reports/technical papers/presentations

"Front-End Engineering Design (FEED) Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Turbine Combined Cycle Power Plant (2x2x1 Duct-Fired 758-MWe Facility with F Class Turbines)," DOE Kick-off Meeting, November 15, 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10905&filename=Front-End+Engineering+Design+(FEED)+Study+for+a+Carbon+Capture+Plant+Retrofit+to+a+Natural+Gas-Fired+Gas+Turbine+Combined+Cycle+Power+Plant.pdf*.

"Front-End Engineering Design (FEED) Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Turbine Combined Cycle Power Plant (2x2x1 Duct-Fired 758-MWe Facility with F Class Turbines)," NETL Project Review Meeting – CCUS Integrated Projects, August 18, 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Elliott.pdf*.

"Front-End Engineering Design (FEED) Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Turbine Combined Cycle Power Plant (2x2x1 Duct-Fired 758-MWe Facility with F Class Turbines)," Final Project Presentation, June 17, 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10904&filename=Front-end+Engineering+Design+(FEED)+Study+for+a+Carbon+Capture+Plant+Retrofit+to+a+Natural+Gas-fired+Gas+Turbine+Combined+Cycle+Power+Plant+.pdf*.

Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation

primary project goal

General Electric Gas Power (GEGP), in collaboration with Linde Inc., Kiewit Engineering Group Inc., and Southern Company Services, is conducting a front-end engineering design (FEED) study for a "Generation 2" amine-based post-combustion carbon capture system integrated with an existing natural gas combined cycle (NGCC) power plant. The system is being designed to capture carbon dioxide (CO_2) emissions with at least 95% efficiency.

technical goals

- Select the NGCC power plant/carbon capture system interfaces to minimize integrated performance loss and advance to 95% from previous 90% CO_2 capture FEED studies, and investigate the impact of exhaust gas recirculation (EGR) on reducing capture cost.
- Complete detailed heat and mass balances, piping and instrumentation diagrams (P&IDs), piping layouts, electrical design, and all other details needed to define the capital/operating costs to support plant-level construction.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA); complete environmental, health, and safety (EH&S) and hazard and operability (HAZOP) reviews of the capture system design; and perform sensitivity studies of CO_2 capture from 90% to as high as 99%.

technical content

The FEED study is focused on a commercial-scale carbon capture plant installed at an existing F-Class NGCC site. GEGP anticipates a high level of system integration that is low-cost, highly efficient, and scalable to other commercial sites.

This is accomplished through advancements in three aligned technology elements:

- Element 1: Amine-based carbon capture with efficiency advanced from 90–95% ("Generation 2").
- Element 2: Comprehensive NGCC/capture system integration with advanced plant-level controls.
- Element 3: EGR technology applied to the gas turbine.

Among the options for post-combustion CO_2 capture from NGCC power plants, liquid solvent-based technologies are currently the most attractive for large-scale commercial application in terms of cost, performance, reliability, and Technology Readiness Level (TRL). However, several challenges still exist for solvent-based technologies. Solvent stability and degradation add to plant operating expenses (OPEX), creating further headwinds in the face of this critical infrastructure development. Offering a superior solution that addresses all these challenges, the Linde-BASF aqueous amine solvent-based carbon capture technology provides the optimal synergy of solvent performance and innovative engineering design

program area:
Point Source Carbon Capture

ending scale:
FEED

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
FEED Study on Amine-Based Solvent Technology Retrofit to NGCC Plant

participant:
General Electric Gas Power (GEGP)

project number:
FE0032131

predecessor projects:
N/A

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partners:
Linde Inc.; Kiewit Engineering Group Inc.; Southern Company Services

start date:
02.11.2022

percent complete:
10%

that minimizes the cost and risk implications of CO_2 capture when deployed at commercial scale. The Linde-BASF technology is based on a typical lean-rich solvent absorption/regeneration cycle for CO_2 capture, but leverages several key innovative features for both solvent and process optimization. A schematic of the Linde-BASF process, including process improvements, are shown in Figure 1.

Linde and BASF have jointly developed and demonstrated advanced CO_2 capture capabilities since 2007. BASF's early solvent development efforts resulted in the formulation of new, next-generation solvents, such as OASE® blue. Linde has improved process design, with CO_2 capture from low-pressure sources, and demonstrated longer stability and a lower solvent circulation rate that further reduces the cost of CO_2 capture from NGCC plants.

The key process components of the Linde-BASF technology are all at TRL 6. This includes absorber/stripper columns, heat exchangers and reboiler, stripper heat integration/recovery, emissions control, and the OASE blue solvent. The TRL 6 is also supported by experimental data, including Linde-modeled external heat integration for carbon capture process (2012); pilot testing (1.5-megawatt-electric [MWe] scale) on coal-fired flue gas in Wilsonville, Alabama, with up to 95% capture efficiency (2014-2016); flue gas aerosol reduction process options tested at Niederaussem for OASE blue solvent (2015); and successful engineering-scale testing of components on 0.45-MWe NGCC-based exhaust gas (2016).

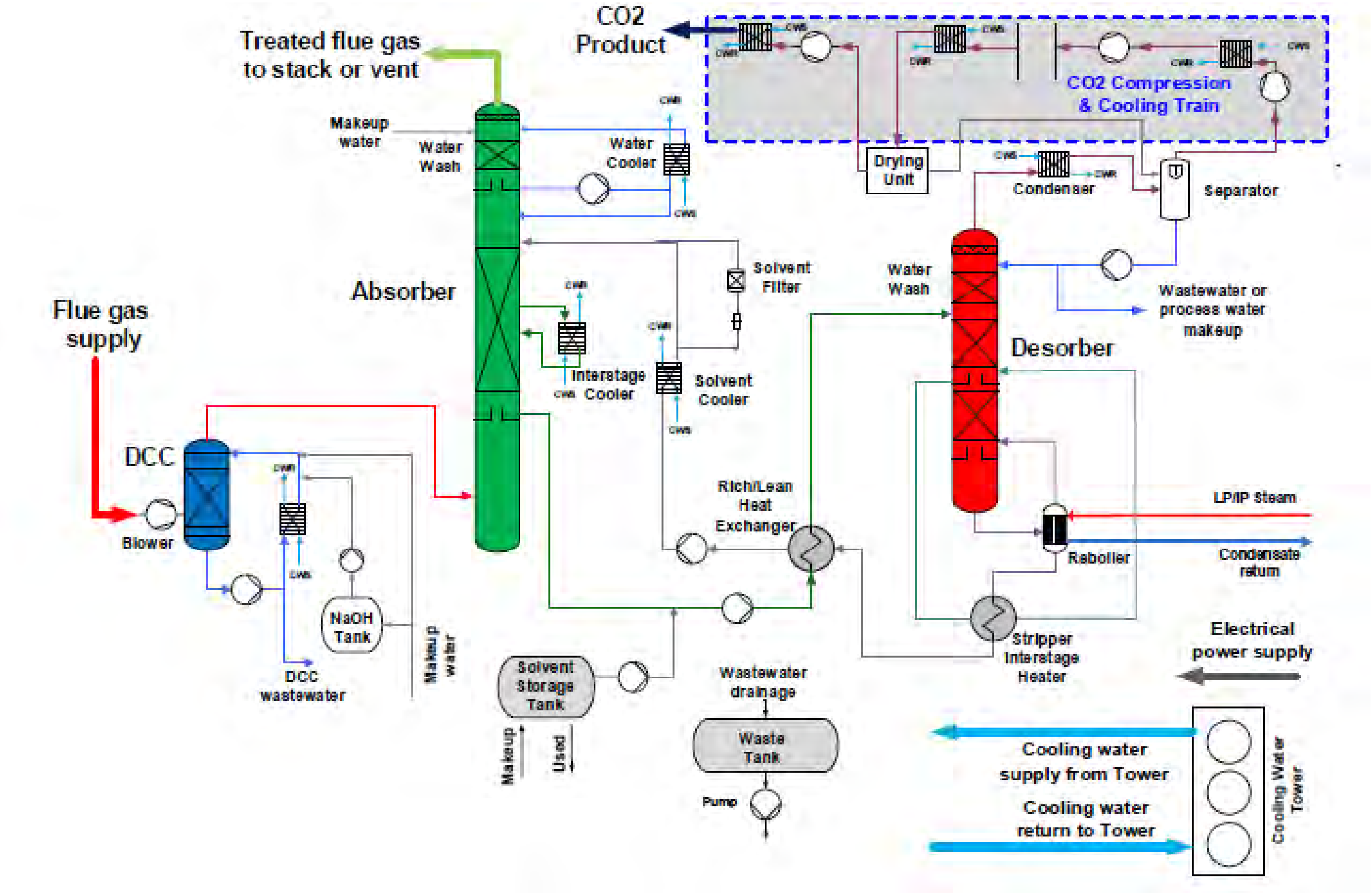

Figure 1: Linde-BASF carbon capture technology.

Description of NGCC Integration

The second element is an NGCC plant-level integration. GEGP has successfully executed gas turbine/combined cycle FEED-related studies for power generation and chemical process industries and oil and gas customers for many years. Examples include application of the first reheat bottoming cycle design, along with the introduction of the F-Class gas turbine, and similar customer plant FEED studies, with its steam-cooled H-Class gas turbine in its early application. GEGP has also been involved with combined cycle power island system designs for integrated gasification combined cycle (IGCC) plants. Examples include the first coal demonstration project in the United States and, more recently, a full-scale IGCC plant in the United States that includes future carbon capture capability. As the complexity of the cycle increases, the need for advanced controls is more critical. With the close dependency of the carbon capture system on the NGCC plant, and vice versa, the need for adaptive, closed-loop, model-based control becomes crucial to maintaining flexible, reliable, and stable operation. This is particularly important during transients caused by changing load or ambient pressure and temperature. The project is identifying and developing key system configurations to enable reliable operation of the NGCC and carbon capture systems, as well as defining a plant operating philosophy to be used by the gas turbine and plant control systems. An optimal configuration includes processes for managing stable and reliable capture system operation at reduced NGCC plant load and NGCC starting/loading. This comprehensive approach yields a more robust solution compared to a piece-meal approach of separate controls for the gas turbine, steam turbine, and carbon capture system. This element also focuses on identifying the optimal location of steam extraction from the existing NGCC power plants, as well as the technically and commercially feasible modifications that should be made to both the steam turbine and the heat recovery steam generator (HRSG) to allow the large steam supply to the carbon capture system. An operability assessment is performed to identify recommended locations of alternate steam supply to allow stable NGCC/carbon capture system operation across a wide range of ambient conditions and plant load demand, including operability of the steam turbine. The second element is at TRL 9, as other equally complicated integration technologies employing advanced controls and bottoming cycle optimization, such as IGCC, have been designed and operated successfully.

Description of Exhaust Gas Recirculation

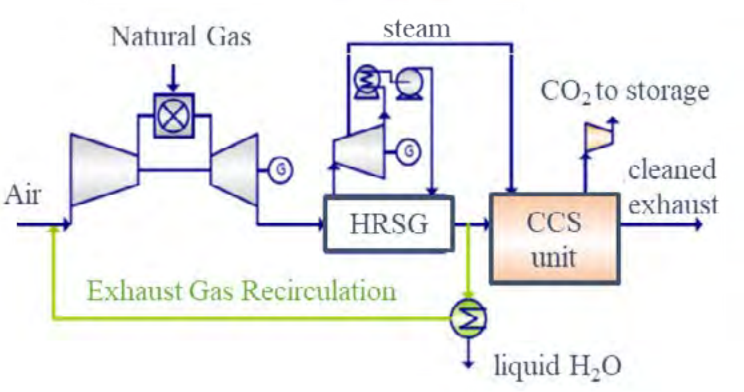

Figure 2: Exhaust gas recirculation.

The third element is the addition of EGR (Figure 2) at the Plant Barry host site located in Bucks Alabama. EGR is a viable and promising option to (a) reduce the exhaust gas flow to the carbon capture system, resulting in cost reductions, and (b) increase the CO_2 concentration in the exhaust gas, resulting in increased capture rate. GEGP has extensively studied EGR since 2006 and anticipates that EGR may be needed to practically achieve carbon capture efficiencies greater than 95%. In 2008, GEGP performed TRL 6-level EGR testing of an F-Class combustor that is the same pre-mixer combustion configuration as that at the Plant Barry host site. These tests confirmed the feasibility of using GEGP's F-Class dry low nitrogen oxide (DLN) combustors in low oxygen conditions with EGR levels up to 30%, potentially up to 40% and higher. These tests also verified that EGR provides increased CO_2 concentrations (>8% CO_2) and reduced nitrogen oxide (NO_X) emissions. These TRL 6-level test results are directly applicable to the Plant Barry FEED study. GEGP is also considering the use of commercially available gas turbine inlet air chilling in the EGR loop for improved plant output. Furthermore, GEGP investigated higher levels of EGR, up to and including Stoichiometric EGR (SEGR) in 2012.

The project begins with various conceptual designs, with a downselect leading to a single NGCC/CCS configuration. The project focuses on system operability to include startup, shutdown, and a range of outputs and loads, which is critical to enable NGCC plants with CO_2 capture to complement renewable power sources. The project concludes with a detailed design, assessment of technical viability across a real-world plant operating profile, TEA and LCA, and a business case assessment.

technology advantages

- Identifies carbon capture system integration and operation risks and recommends solutions to eliminate or manage the risks.

R&D challenges

- Identifying the optimal location of steam extraction from the existing NGCC power plants.

status

The project began on February 11, 2022. GEGP is working on down selecting an optimal NGCC/capture system configuration and assessing the viability of EGR integrated into the design.

available reports/technical papers/presentations

Sholes, J., "Retrofittable Advanced Combined Cycle Integration for Flexible Decarbonized Generation," Project kickoff meeting presentation, March 2022. *https://netl.doe.gov/projects/plp-download.aspx?id=13050&filename=Retrofittable+Advanced+Combined+Cycle+Integration+for+Flexible+Decarbonized+Generation.pdf*.

Commercial-Scale Front-End Engineering Design Study for Membrane Technology and Research's Membrane Carbon Dioxide Capture Process

primary project goal

Membrane Technology and Research, Inc. (MTR) is conducting a front-end engineering design (FEED) study for an ~400-megawatt-electric (MWe) membrane-based carbon dioxide (CO_2) capture system installed at Basin Electric's Dry Fork Station in Gillette, Wyoming. The project builds on prior work in advancing MTR's membrane capture technology through small pilot testing and a pre-FEED study.

technical goals

- Complete FEED study of MTR capture process applied to the 400-MWe Dry Fork Station.
- Complete an environmental review of full-scale MTR membrane capture at Dry Fork Station.
- Provide a path to commercialization (detailed costs and construction plan) for a full-scale membrane capture plant based on actual equipment costs with a reliability of ±15%.

technical content

The project team is performing a FEED study of MTR's membrane CO_2 capture technology applied at commercial-scale as the next step in the development of the process, after the successful completion of small pilot testing and execution of a full-scale pre-FEED study. The study includes an estimate of the cost and performance of a first-of-its-kind commercial-scale membrane capture plant and a plan for its construction. The plant is being designed to capture approximately 5,600 tonnes per day (TPD) of CO_2 (approximately 2.0 million tonnes/year of CO_2), representing 70% of the Dry Fork Station power plant's CO_2 emissions. The system incorporates the innovative high-performance Polaris™ membrane packaged in low-pressure-drop membrane modules. Earlier research has shown that the MTR process has the potential to capture CO_2 from coal-fired flue gas at the U.S. Department of Energy (DOE) capture cost target of less than $40/tonne CO_2.

A preliminary process flow diagram of the membrane capture process to be examined in the FEED study is shown in Figure 1.

program area:

Point Source Carbon Capture

ending scale:

FEED

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Polaris™ Polymeric Membrane-Based Process Retrofit to Coal Plant

participant:

Membrane Technology and Research, Inc.

project number:

FE0031846

predecessor projects:

FE0026414
DE-NT0005312
FC26-07NT43085
FE0005795
FE0007553
FE0013118

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partners:

Sargent & Lundy (S&L); Basin Electric; Trimeric Corporation; Electric Power Research Institute (EPRI); Efficient Fuel Additives (EFA)

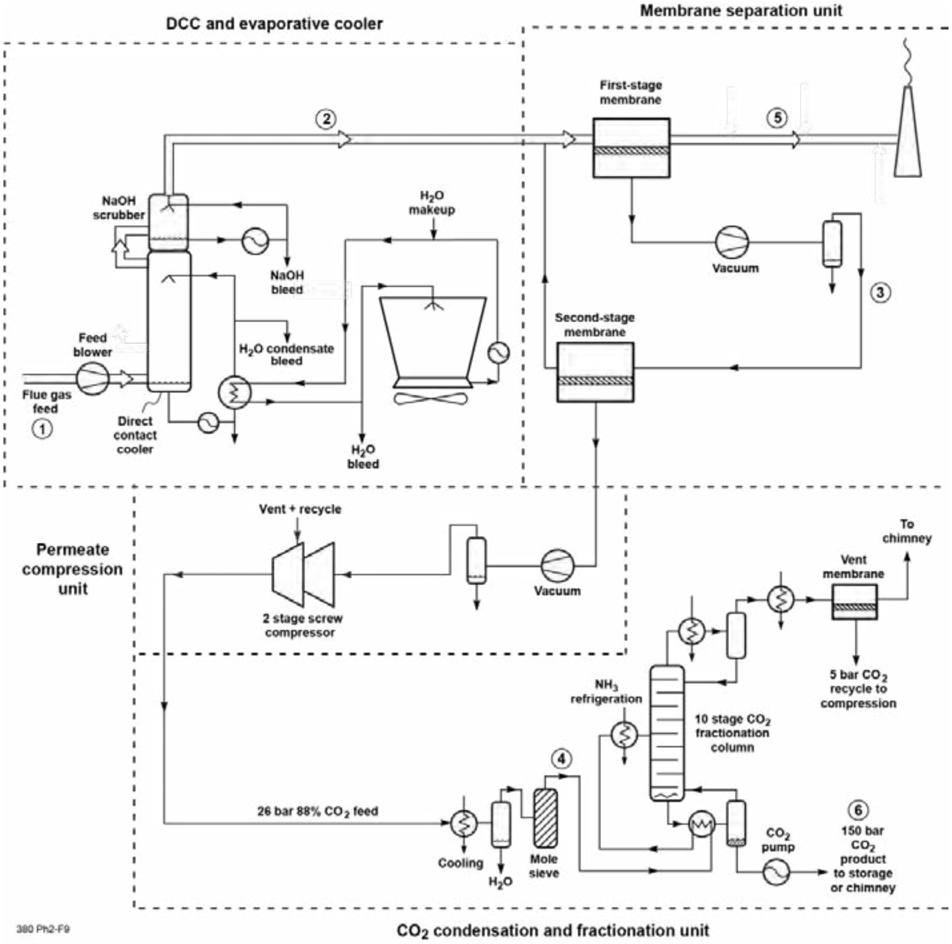

Figure 1: Preliminary design for full-scale membrane capture plant.

Compared to other industrial membrane applications, the main challenge of membrane technology for post-combustion CO_2 capture is the low partial pressure of CO_2 in flue gas, resulting in a large membrane area being required due to the small driving force for separation. MTR has developed two innovations that address this problem:

- A new class of membranes called Polaris that exhibit 10 times the CO_2 permeance of conventional gas separation membranes, leading to a large decrease in required membrane area and reduced capital cost.
- A low-pressure-drop, low-cost membrane module design. The pressure differentials, and therefore the energy required, to circulate gas through the module is a fraction of that measured in conventional modules.

Single-stage membrane designs are unable to produce high-purity CO_2 combined with high CO_2 capture rates because the system performance is limited by the small pressure ratio across the membrane. MTR's multi-stage membrane process design (Figure 2) addresses the pressure ratio constraint to efficiently capture 50 to 75% of the CO_2 in flue gas. First, the combustion flue gas enters a primary capture module, which produces a permeate containing ~55 to 60% CO_2. This gas is then treated by a second membrane stage to further enrich the CO_2 stream to greater than 85% CO_2. The CO_2-rich permeate from the second-stage module is dehydrated and compressed.

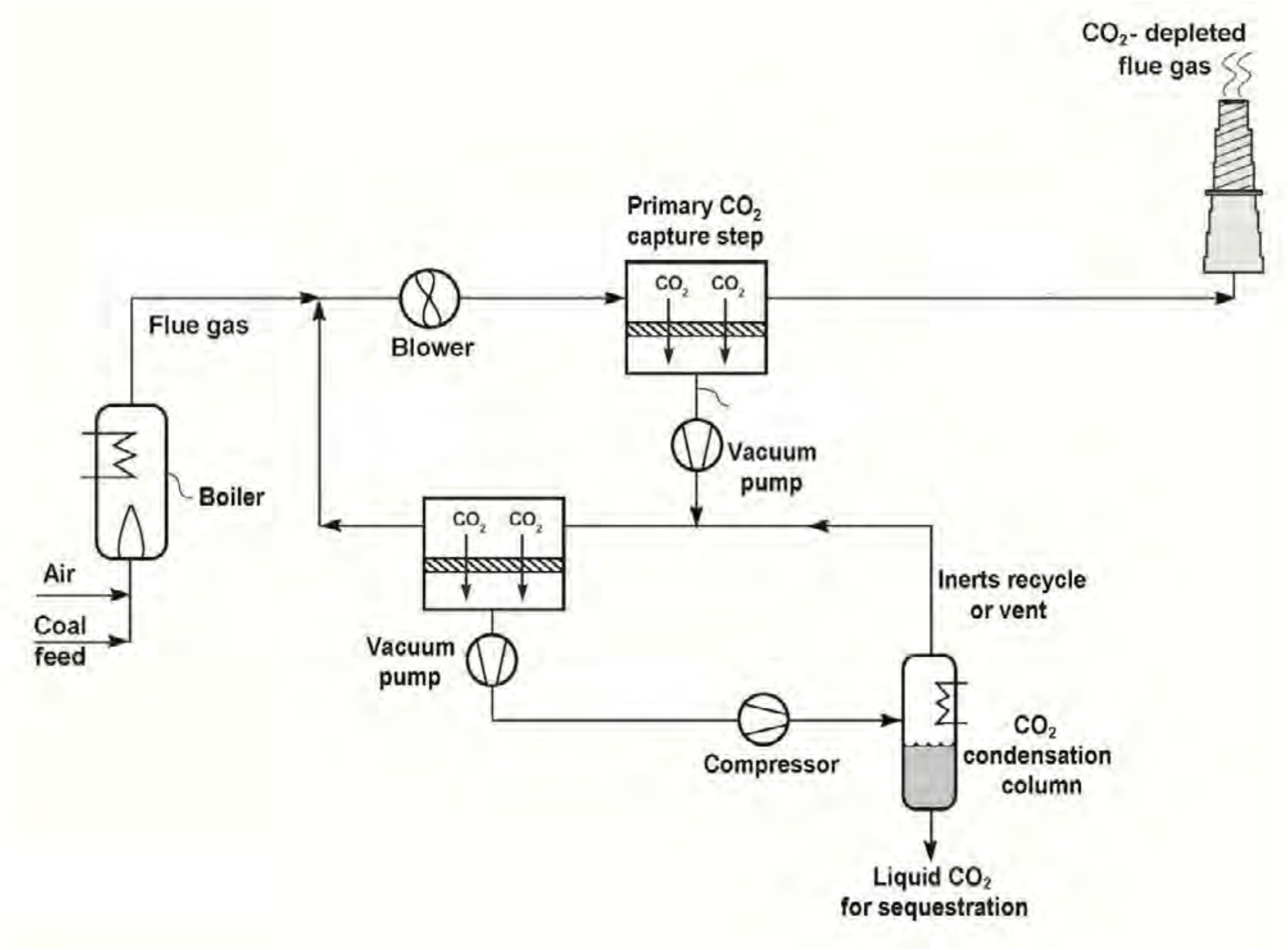

Figure 2: MTR CO_2 capture process.

MTR's Polaris membrane was first developed in a previous DOE-funded project, DE-NT43085. Polaris exhibits high CO_2 permeance and high CO_2/nitrogen (N_2) selectivity for post-combustion flue gas applications. The thin-film composite membrane utilizes hydrophilic polymers. Commercial Polaris membranes offer a step-change improvement over typical commercial CO_2-selective membranes used for natural gas treatment, with an average CO_2 permeance of 1,000 gas permeation units (GPU) and a CO_2/N_2 selectivity of 50. Recent studies have improved membrane performance, demonstrating a CO_2 permeance of 3,000 GPU at lab-scale. The combination of these membranes with novel module and process innovations greatly reduces the projected cost of CO_2 capture.

Membranes packed into spiral-wound modules are widely used in commercial membrane installations today. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 3 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, which allow the flue gas and separated CO_2 to flow through the device. The process parameters for the Polaris membranes in a spiral-wound module configuration are shown in Table 1.

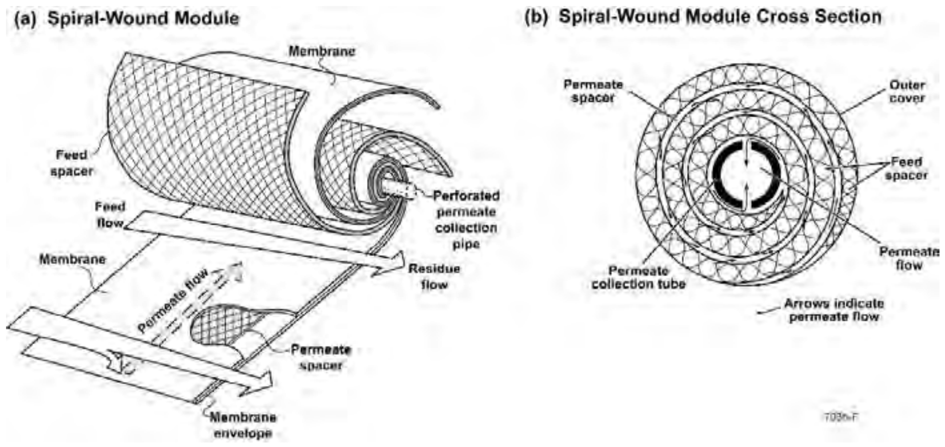

Figure 3: Schematic diagram of a spiral-wound membrane module.

TABLE 1: MEMBRANE PROCESS PARAMETERS IN SPIRAL-WOUND MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	spiral
Max Trans-Membrane Pressure	bar	70
Hours Tested without Significant Degradation	—	11,000
Manufacturing Cost for Membrane Material	$\$/m^2$	10
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,000
CO_2/H_2O Selectivity	—	0.3
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow and countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flowrate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >96% / 140
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Under a previous DOE-funded project, DE-FE0005795, a membrane skid designed to capture 1 tonne of CO_2 per day from a 7,000-standard-m^3/day (250,000 standard cubic feet per day [scfd]) flue gas slipstream was installed and tested at the National Carbon Capture Center (NCCC; Figure 4). The skid held up to eight (four crossflow and four countercurrent sweep), 8-inch-diameter Polaris membrane modules. The system accumulated more than 11,000 hours of operation with flue gas testing spiral-wound modules in both steps of the MTR process: a capture step operating with permeate vacuum and a selective-recycle step that uses air sweep to provide driving force for CO_2 removal. The test demonstrated membrane operation in commercial-scale modules and determined typical membrane lifetimes under coal combustion flue gas operating conditions.

Figure 4: Membrane skid used for 1-TPD bench-scale slipstream testing at NCCC.

Scale-up of the Polaris capture system from the 1-TPD bench-scale unit to a 20-TPD small pilot system using commercial-scale membrane components was also completed in FE0005795. The 20-TPD system is a two-level design, with membrane modules located on the upper level, and all rotating and associated equipment on the lower level. Like the 1-TPD unit, the 20-TPD unit was designed for slipstream operation at NCCC and is shown in Figure 5.

Figure 5: 20-TPD small pilot system installed at NCCC.

Pilot-scale operation of the previous 1-MWe (20-TPD) membrane CO_2 capture system, integrated with a Babcock & Wilcox (B&W) 0.6-MWe coal-fired research boiler, was performed in the DOE-funded project DE-FE0026414 to determine how various membrane parameters impact the performance of a boiler system. Operation of the integrated membrane-boiler system involves the recycling of CO_2-laden air back to B&W's boiler via a countercurrent sweep membrane. A modest reduction in boiler efficiency due to recycled CO_2 was measured (1.8%) at 90% capture, showing that the selective-recycle process is feasible and the impact on boiler performance is relatively small.

While previous tests have shown that recycle to the boiler is feasible, operation at ~70%+ capture without recycle is often of interest, because it offers lower capture costs and still reduces coal plant emissions to less than that of a natural gas power plant. Therefore, the current FEED study focuses on a two-stage membrane system that captures 70% of the CO_2 in the flue gas without selective recycle and concentrates the gas to about 85% CO_2. A CO_2 purification unit is then used to produce greater than 99% CO_2 at 150 bar. For the full-scale capture plant, container-sized skids will be used as the basic modular building block. An evaluation of the most efficient arrangement of the membrane capture skids is being conducted in the FEED study.

MTR applied an alternative approach to membrane packing to develop planar modules optimized for low-pressure operation. Testing of the small pilot-scale 20-TPD system at NCCC and B&W incorporated this novel large-area membrane module designed by MTR in project DE-FE0007553. A single planar membrane module element has the equivalent membrane area of five 8-inch spiral-wound membrane modules. Figure 6 shows the plate-and-frame module design. The simple, straight flow path of the new module design results in a pressure-drop that is almost four times lower than that measured for the spiral-wound module, as shown in Figure 7, resulting in energy and cost savings. At full-scale, this reduced pressure-drop represents about a 10-MWe savings in fan power. The planar module skids are projected to cost \$50/m^2 of membrane at full commercialization stage. Process parameters for the Polaris membranes in a planar module configuration are shown in Table 2.

Figure 6: Prototype plate-and-frame module during testing at NCCC.

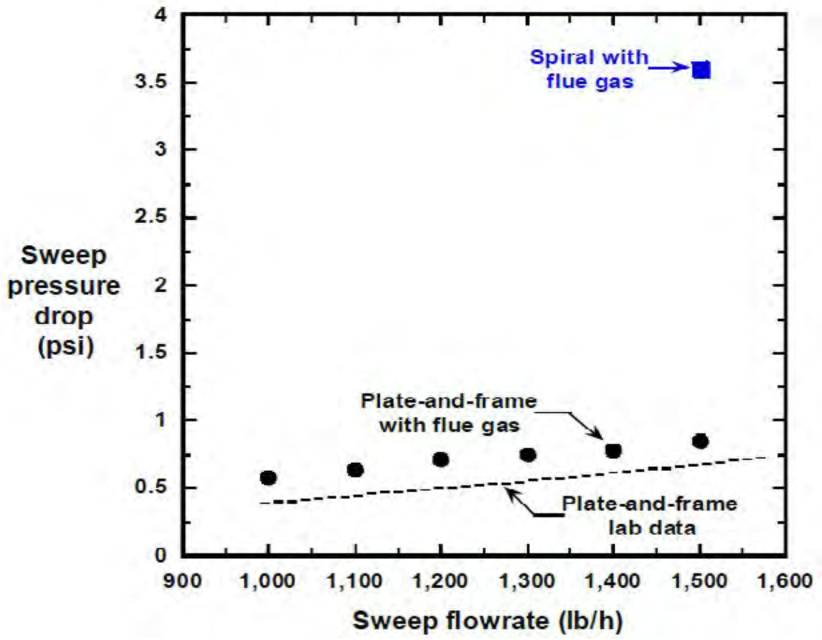

Figure 7: Measured pressure-drop in plate-and-frame module, compared to spiral-wound module.

TABLE 2: MEMBRANE PROCESS PARAMETERS IN PLATE-AND-FRAME MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	plate-and-frame
Max Trans-Membrane Pressure	bar	2
Hours Tested without Significant Degradation	—	1,500
Manufacturing Cost for Membrane Material	$\$/m^2$	30
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,700
CO_2/H_2O Selectivity	—	0.5
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow, partial countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flowrate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70% / >96% / 150
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Further improvements to the membrane module design to reduce fabrication costs resulted in a module prototype based on injection-molded, fiber-reinforced thermoplastics. The modules are designed to fit one on top of another to create a module stack, which is placed on a container-sized skid, as shown in Figure 8. The large membrane capture system will consist of multiple container-sized membrane module skids that will be prefabricated using advanced, high-volume manufacturing and shipped to the plant site. This approach minimizes expensive site assembly and installation work and enhances fabrication quality. The FEED study is evaluating and quantifying savings based on the modular construction approach.

Figure 8: Containerized plate-and-frame membrane module stacks.

MTR also previously evaluated a hybrid membrane-absorption process system combining Polaris membranes and an amine solvent-based capture system under DOE-funded project DE-FE0013118. The integrated system combines MTR's plate-and-frame sweep module with a CO_2 capture system developed by the University of Texas at Austin (UT-Austin) that uses a piperazine (PZ) solvent and advanced high-temperature/high-pressure regeneration. This hybrid design requires significantly less membrane area for a two-step CO_2 capture process, compared to MTR's all-membrane process. In the hybrid design, MTR's Polaris membrane recycle stage enriches flue gas from ~13 to ~20% CO_2 and a 5 molal PZ advanced flash stripper with cold-rich bypass is optimized to take advantage of the higher CO_2 concentration. Both series and parallel configurations were considered with the hybrid design, as shown in Figure 9. Process modeling of MTR's plate-and-frame skid integrated with UT-Austin's Separations Research Program (SRP) 0.1-MWe pilot plant showed that a hybrid-parallel configuration offers a lower cost of capture than the series configuration. However, the benefits of a hybrid system do not outweigh the costs. The estimated economics data, including cost of capture, is shown in Table 3.

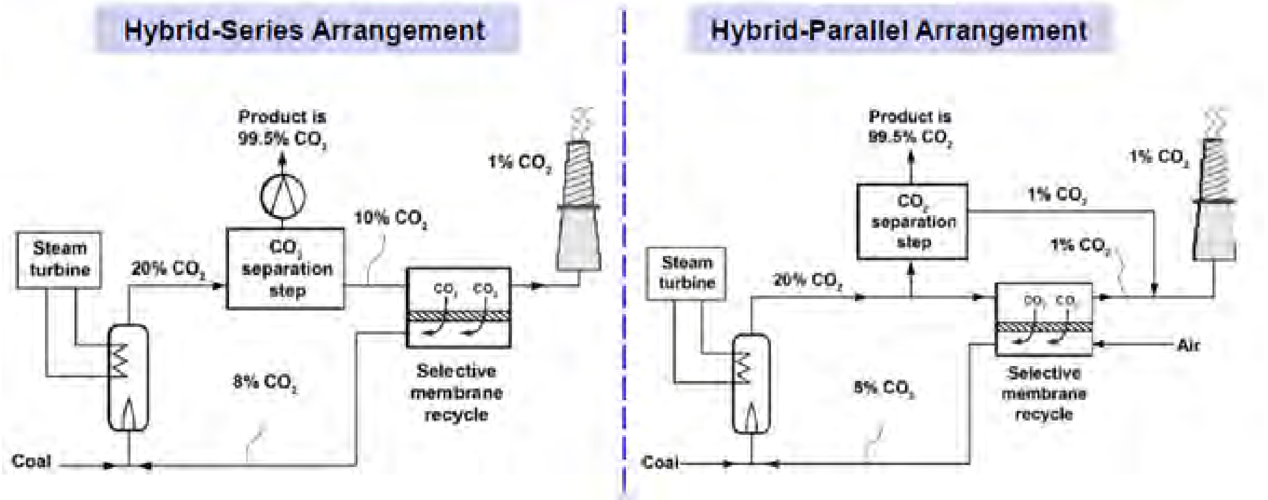

Figure 9: Two hybrid configurations for membrane-absorption CO_2 capture process.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	n/a	n/a
Capital Expenditures	\$/MWhr	18.4	23.9
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/kWhr	0.05	0.05

MTR is also currently working on three additional DOE-sponsored projects related to this study. DE-FE0031587 is a three-phase project for the design, construction, and operation of a large-scale pilot system to treat 10 MWe of flue gas at Wyoming's Integrated Test Center, with support from Basin Electric's Dry Fork Station power plant. The Phase I feasibility program and the Phase II FEED study are complete and the project is now in Phase III. The National Environmental Policy Act (NEPA) review and Environmental Information Volume (EIV) that were completed in Phase I can be leveraged in this FEED project. The second project recently completed (DE-FE0031589) is a pre-FEED study led by the Electric Power Research Institute (EPRI), in collaboration with MTR, Nexant, and Bechtel, to evaluate a full-scale (640-MWe) membrane capture technology applied to Duke Energy's East Bend Station. The general configuration from the pre-FEED capture plant design is being used as the starting point for the Dry Fork Station FEED study. In project DE-FE0031591, MTR and its partners are scaling-up the next-generation Polaris membranes and modules to a final form optimized for commercial use, and validating their performance in an engineering-scale field test at Technology Centre Mongstad.

The Dry Fork Station power plant is an ideal location for installation of a membrane CO_2 capture system due to:

- High CO_2 content (~15% on dry basis) in the flue gas increases efficiency of membrane capture system.
- Cool, dry climate allows cooling water operation at ~25°C, resulting in an energy savings of 25 MWe/tonne of CO_2 captured.
- Dry Fork Station generates electricity at a low cost, which is important for a capture process powered only by electricity.
- CO_2 utilization opportunities with nearby oil fields and CO_2 pipeline.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed- or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., was examined in the field tests at NCCC and no major issues were found.

Flue Gas Pretreatment Requirements – The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. The field tests at NCCC treated post-FGD flue gas, and in extended testing (more than 13,000 hours), fouling was not a significant issue.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

Process Design Concept – See Figure 1.

technology advantages

- The Polaris membranes developed are more than 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The membrane material has a high tolerance to wet acid gases and is inert to O_2.
- The membrane system has a flexible footprint and low energy cost.
- The membrane capture system can recover water from flue gas.
- The use of an existing air stream to generate a CO_2 partial-pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO_2 from the air sweep to the boiler increases the CO_2 partial-pressure driving force for separation in the initial CO_2 separation step (either membrane or absorption/stripper unit), reducing total system cost.

R&D challenges

- Uncertainty in vacuum pumps and compression equipment efficiency and stability treating flue gas.
- Potential performance problems with the CO_2 purification equipment.
- Scale-up of advanced Polaris membranes that exhibit a CO_2 permeance of 3,000 GPU to reduce the capital cost of the membrane system.

status

MTR has completed all preliminary process design work for the capture plant. All operating parameters have been defined and all vendor equipment has been selected. In addition, a waste management plan has been finalized, and the detailed equipment arrangement within the plant is currently being developed. The remaining balance of plant and building designs, as well as cost estimates, are also under development.

available reports/technical papers/presentations

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Initial Engineering, Testing, and Design of a Commercial-Scale, Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit

primary project goals

The University of North Dakota Energy and Environmental Research Center (EERC), in partnership with the North Dakota Industrial Commission, ALLETE Clean Energy, Minnkota Power Cooperative, Mitsubishi Heavy Industries (MHI), and Burns & McDonnell, completed a pre-front-end engineering and design (pre-FEED) analysis and cost estimate for retrofitting MHI's Kansai Mitsubishi Carbon Dioxide Recovery (KM-CDR™) amine-based post-combustion carbon dioxide (CO_2) capture process with an existing coal-fired generating unit.

technical goals

The goal of the project was to determine retrofit costs for a post-combustion CO_2 capture system on an existing coal-fired electric generating unit. Specific objectives to support this goal included:

- Designing a fully integrated post-combustion CO_2 capture system for Milton R. Young Unit 2 (MRY2).
- Evaluating KS-1™ solvent on lignite coal-derived flue gas to refine critical design parameters.
- Completing a techno-economic assessment (TEA) in accordance with the U.S. Department of Energy's (DOE) bituminous baseline study (B12B).
- Completing a pre-FEED analysis of the specified post-combustion CO_2 capture system at MRY2.

technical content

The commercially available KM-CDR process uses an advanced amine solvent, KS-1, that exhibits less solvent degradation, a higher working capacity and lower solvent circulation rate, and reduced steam consumption for regeneration compared to monoethanolamine (MEA). The solvent technology has shown to be reliable, routinely achieving 90% CO_2 removal, while capturing approximately 1.6 million tonnes of CO_2 per year from a 240-megawatt-electric (MWe) sub-bituminous coal-derived flue gas stream at the W.A. Parish Plant in Thompsons, Texas, through a DOE-funded project with Petra Nova Parish Holdings LLC. Through the development, several improvements to the process have been implemented, including a novel flue gas quencher and absorber design for lower capital costs and ease of construction and an amine wash section for minimizing aerosol emissions from treated flue gas. The team designed a fully integrated KM-CDR system for installation at MRY2 near Center, North Dakota; performed testing with EERC's slipstream baghouse installed at MRY2 to evaluate aerosol emissions; evaluated the KS-1 solvent on lignite coal-derived flue gas to refine critical design parameters; completed a TEA in accordance with DOE's B12B; and completed a pre-FEED analysis and cost estimate of the system at MRY2.

program area:

Point Source Carbon Capture

ending scale:

Pre-FEED

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

KM-CDR™ Process Coal-Fired Retrofit Pre-FEED

participant:

University of North Dakota Energy and Environmental Research Center (EERC)

project number:

FE0031602

predecessor projects:

N/A

NETL project manager:

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principal investigator:

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partners:

North Dakota Industrial Commission; ALLETE Clean Energy; Minnkota Power Cooperative; Mitsubishi Heavy Industries (MHI); and Burns & McDonnell

start date:

06.05.2018

percent complete:

100%

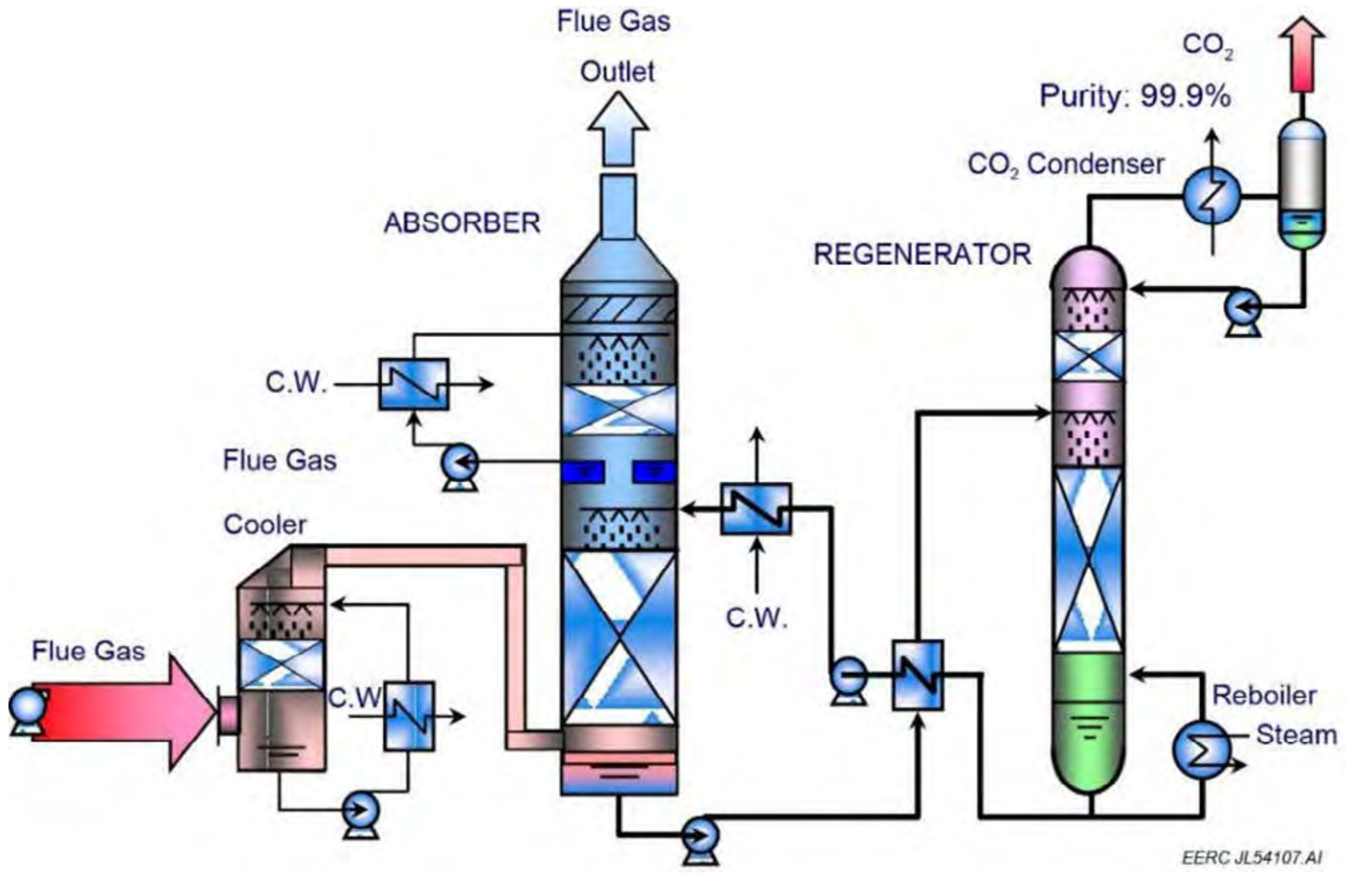

Figure 1: MHI's KM-CDR™ process.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary data	proprietary data
Normal Boiling Point	°C	proprietary data	proprietary data
Normal Freezing Point	°C	proprietary data	proprietary data
Vapor Pressure @ 15°C	Bar	proprietary data	proprietary data
Manufacturing Cost for Solvent	$/kg	proprietary data	proprietary data
Working Solution			
Concentration	kg/kg	proprietary data	proprietary data
Specific Gravity (15°C/15°C)	-	proprietary data	proprietary data
Specific Heat Capacity @ STP	kJ/kg-K	proprietary data	proprietary data
Viscosity @ STP	cP	proprietary data	proprietary data
Absorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data
Heat of Absorption	kJ/mol CO_2	proprietary data	proprietary data
Solution Viscosity	cP	proprietary data	proprietary data
Desorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data

Heat of Desorption	kJ/mol CO_2	proprietary data	proprietary data
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,938,700	
CO_2 Recovery, Purity, and Pressure	% / % / bar	95% / 99.9%+ / 158.6	
Absorber Pressure Drop	Bar	proprietary data	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary data	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%-wet					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_2**	**NO_x**
13.68	150	10.45	20.5	62.9	5.3	0.79	44	149.7

Chemical/Physical Solvent Mechanism – Carbon dioxide is captured by chemical absorption.

Solvent Contaminant Resistance – KS-1 solvent is highly resistant to contaminant compared to conventional solvent MEA.

Solvent Foaming Tendency – KS-1 solvent has low foaming tendency compared to conventional solvent MEA.

Flue Gas Pretreatment Requirements – Flue gas cooling and sulfur oxide (SO_X) removal unit may be required depending on flue gas conditions.

Solvent Makeup Requirements – Solvent makeup rate depends on the impurity levels in the flue gas but is generally lower than conventional solvent MEA.

Waste Streams Generated – Solvent reclaiming waste is the main waste stream generated.

Process Design Concept – KM-CDR process is equipped with a proprietary amine emissions reduction system, energy-saving system, and amine purification system, which maximize the capture efficiency while minimizing the energy consumption and environmental impact.

Proposed Module Design – Not applied.

technology advantages

The combination of the state-of-the-art KM-CDR technology with refined design criteria and optimized thermal integration improved the performance of the CO_2 capture system and maximized overall system efficiency.

- The Plant Barry 25-MW demonstration facility was operated for more than 12,000 hours and routinely achieved more than 90% CO_2 removal from the coal-derived flue gas stream.

R&D challenges

This project addressed challenges associated with a full-scale system, such as the use of lignite coal, effects from cold climate, treating higher quantities of flue gas, and application of heat integration.

- Cooling water temperature was an important parameter where excessive heating during North Dakota summer led to decreased CO_2 capture percentage by up to 20%.
- Metals concentrations in the solvent increased over time.
- Aerosols entering baghouses led to release during bag-cleaning cycles. It is unknown what impact multi-chambered systems will have on aerosol release with larger systems.

status

Field testing at MRY2 was completed, including long-term stable operation and aerosol mitigation testing. The project design basis was completed, including utility requirements, flow diagrams, balance of plant, permitting strategy, and optimization studies. The project TEA was completed. The project final report was completed, including the pre-FEED cost estimate, system layout, a hazard and operability study (HAZOP), constructability, the steam integration report, the transportation study, and the technology maturation plan.

available reports/technical papers/presentations

Laumb, J., Initial Engineering, Testing, and Design of a Commercial-Scale Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit, Aug 2018, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://www.netl.doe.gov/sites/default/files/netl-file/J-Laumb-UNDEERC-Engineering-Testing-and-Design.pdf*.

Laumb, J., Initial Engineering, Testing, and Design of a Commercial-Scale Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit, Aug 2019, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://netl.doe.gov/sites/default/files/netl-file/J-Laumb-UND-EERC-Postcombustion-Coal-Plant-Capture.pdf*.

Laumb, J. Initial Engineering, Testing, and Design of a Commercial-Scale Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit, Feb 2020 NETL CO_2 Capture Technology, Final Project Review Meeting, Pittsburgh, PA, *https://netl.doe.gov/projects/plp-download.aspx?id=10479&filename=Initial+Engineering%2c+Testing+and+Design+of+a+Commercial-Scale+Post-Combustion+CO2+Capture+System+on+an+Existing+Coal-Fired+Generating+Unit.pdf*.

Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station Using Membrane-Based Technology

primary project goal

The Electric Power Research Institute, Inc. (EPRI) produced an initial engineering design and cost estimate of a first-of-a-kind (FOAK), full-scale, membrane-based post-combustion carbon dioxide (CO_2) capture system retrofit to an existing U.S. coal power plant. The capture technology was provided by Membrane Technology and Research (MTR), and the power plant was Duke Energy's East Bend Station (EBS) located on the Ohio River in Kentucky. The primary objective was to develop a design that would minimize the impact on the power plant by disrupting as little of the existing facilities as possible, minimizing the cost of each tonne of captured CO_2 while also maintaining the net 600-megawatt (MW) output of EBS. This was to be done by optimizing the percentage of CO_2 captured from the coal-fired power plant (expected to be somewhere between 45 and 75% of the total CO_2 in the flue gas). The initial phase was also to examine options for integrating waste heat from the new combustion turbine (CT) with the existing coal plant to improve the thermal efficiency of the coal-fired unit. Once an optimal configuration was selected, an engineering design, sufficient in detail to support a +/-30% capital cost estimate, was to be generated, along with a techno-economic analysis (TEA).

technical goals

- Develop, review, and approve a design basis document for EBS.
- Develop a steam cycle model of an existing power plant and benchmark existing performance.
- Optimize the configuration of the membrane CO_2 capture system, including a decision on the level (percentage) of capture for the design that offers the lowest cost on a $/tonne of CO_2 captured basis.
- Evaluate options for supplying auxiliary power to the CO_2 capture system.
- Develop a complete process design package of the membrane-based CO_2 capture system.
- Define retrofit modifications required to integrate the membrane-based process into EBS and conduct a hazard identification (HAZID)/constructability review of a retrofitted capture facility.
- Complete a TEA for the retrofitted power plant.

technical content

For this retrofit design project, second-generation Polaris™ membranes from MTR and an optimized level of CO_2 capture were used to reduce capture costs, toward a goal of $30/tonne CO_2. These second-generation Polaris™ membranes have double the CO_2 removal capacity of the original membrane and were packaged in low-pressure-drop modules optimized for high-volume flue gas treatment. Prototypes of these modules had been validated in prior field trials that confirm

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polymeric Membrane-Based Process Retrofit Pre-FEED Study

participant:
Electric Power Research Institute, Inc.

project number:
FE0031589

predecessor projects:
N/A

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partners:
Membrane Technology and Research, Inc.; Duke Energy; Nexant Inc.; Bechtel Inc.; Trimeric Corporation

start date:
04.06.2018

percent complete:
100%

large energy and cost savings. Targeting a lower degree of capture for this proposed project will obtain a post-combustion CO_2 capture system that provides the lowest cost on a \$/tonne CO_2 captured basis. Membrane-based post-combustion CO_2 capture systems achieve an optimal cost in the range of 45 to 75% capture.

Duke Energy's EBS was the host site for the retrofit study (Figure 1). EBS is a 600-MW-net coal-fired power plant located on a 1,600-acre site along the Ohio River in Boone County, Kentucky. Duke originally envisioned having multiple 600 megawatt-electric (MWe) units at this site, but only one unit was built. As a result, there is an abundance of space around the existing facility, which will facilitate the addition of the CO_2 capture plant.

Figure 1: Duke Energy's East Bend Station 600-MWe coal-fired power plant.

The proposed design for the EBS post-combustion CO_2 capture system is shown in Figure 2. It is a two-stage membrane system that accomplishes 60% CO_2 capture from the base plant's exhaust, with no boiler recycle.

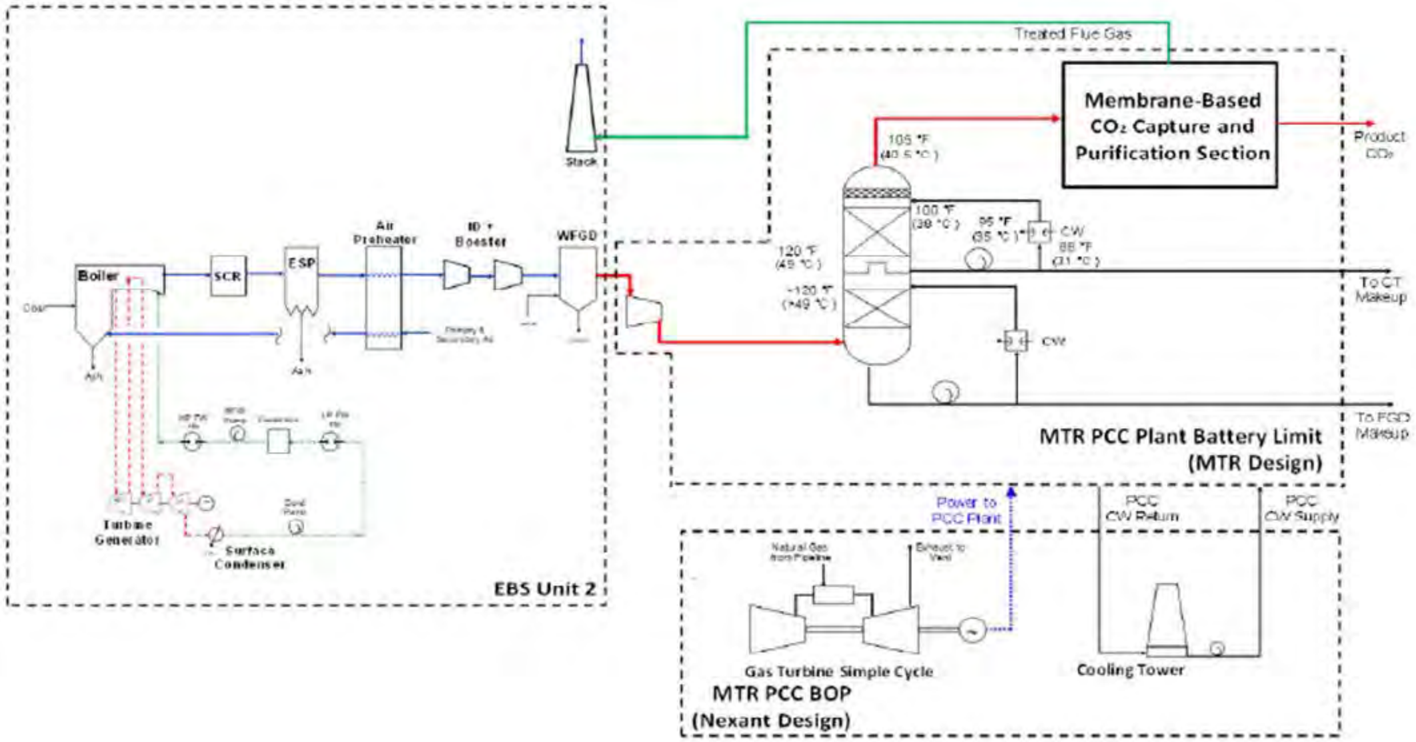


Figure 2: Proposed design for the East Bend unit.

Unlike solvent post-combustion CO_2 capture systems, there is no steam requirement for the membrane system. However, power is required to drive the membrane system's fans, blowers, vacuum compressors, pumps, and CO_2 compressors. To make up for the increased auxiliary load imposed by the post-combustion CO_2 capture system, and to minimize the disruption to the existing power plant, the addition of a natural gas-fired CT power plant to the EBS site was investigated. Various design parameters for the membrane system are shown in Table 1.

Four integration options were considered to provide power to the optimized membrane system retrofit:

1. New natural gas-fired simple cycle (maintain original net output).
2. New combined cycle (maintain original net output).
3. New simple cycle with additional waste heat recovery unit sized to supplying steam to power plant feedwater heaters.
4. Auxiliary power supplied from existing station (decrease net output).

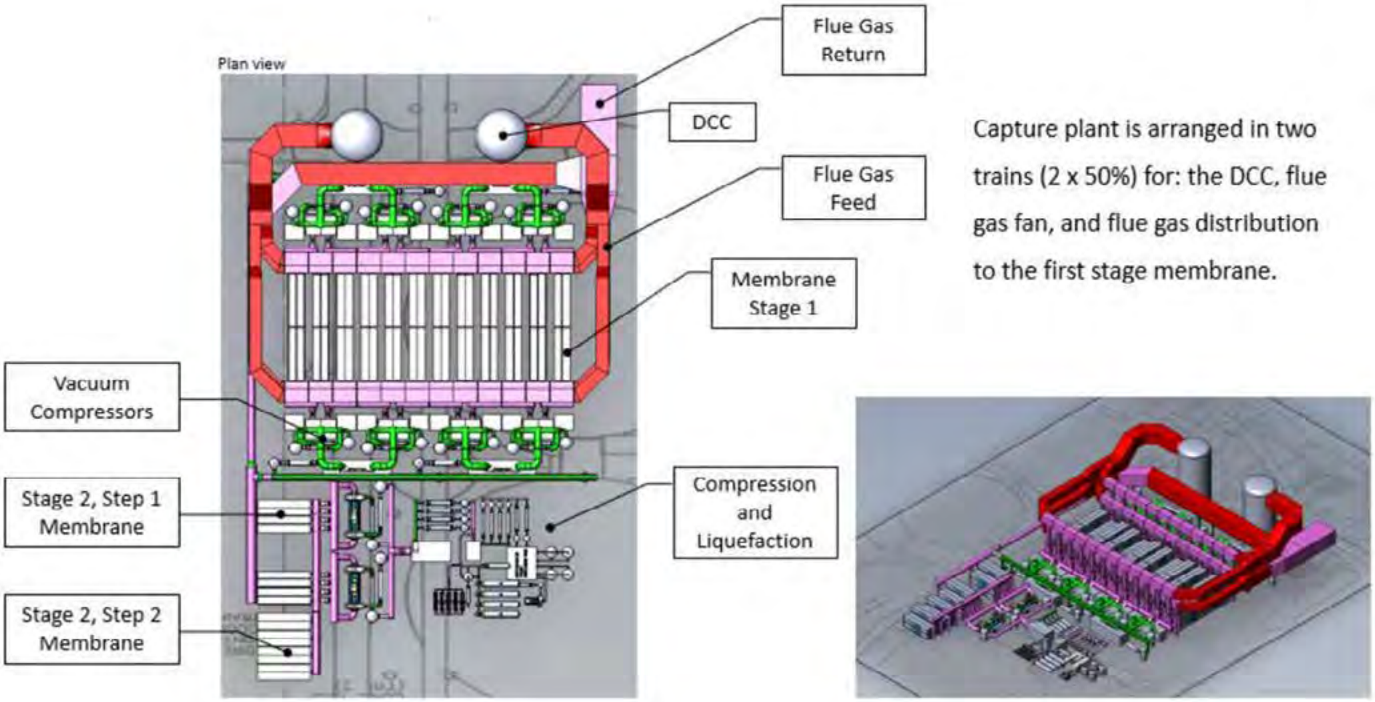
Option 1 with the MTR post-combustion CO_2 capture plant supported by a single gas turbine simple cycle (GTSC) power island was determined to be the best arrangement for this project. It was found to provide:

- The lowest upfront cost of all the external power options considered.
- A phased implementation of feedwater pre-heat if required later (phase in Option 3 if required).
- Enough temperature and heat available for future EBS high-pressure feedwater preheating, if desired.
- Potential for future retrofit with full-size heat recovery steam generator (HRSG) for additional power export if New Source Review (NSR) regulations are relaxed.
- A well-established commercial operation history.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	11,000 (coal)	11,000 (coal)
Manufacturing Cost for Membrane Material	$\$/m^2$	50-100	50-100
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,600	1,600
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Actual flue gas	Actual flue gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	2,661,428	
CO_2 Recovery, Purity, and Pressure	%/%/bar	50-70%, >99%, 153 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.025	

The final proposed membrane process equipment and plant layout detail is shown in Figure 3, and detailed cost of CO_2 data is shown in Table 2.



Capture plant is arranged in two trains (2 x 50%) for: the DCC, flue gas fan, and flue gas distribution to the first stage membrane.

Figure 3: Final proposed membrane process equipment and layout.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured (1)	$/tonne CO_2	75	~30
Cost of Carbon Avoided	$/tonne CO_2	112	n/a
Capital Expenditures	$/MWhr	24	n/a
Operating Expenditures	$/MWhr	28	n/a
Cost of Electricity (2)	$/MWhr	52	n/a

Notes:
(1) Current R&D value based on final pre-FEED study results for specific FOAK East Bend retrofit. (Target R&D value based on initial proposal goal.)
(2) Additional first-year cost of electricity (COE) based on 90% capacity factor.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

HAZID – Hazard Identification study, which was conducted to assess the safety of the post-combustion capture facility at EBS. The study was conducted based on process flow diagrams developed as a part of the previous TEA.

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation occurs by a passive, solution-diffusion process. Permeation driving force through the first-stage membrane module is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

Contaminant Resistance – Very fine particulates flow through the membrane channels and are discharged to the stack. Nitrogen oxides (NO_X) will not harm the membranes. The sulfur oxides (SO_X) that reach the membrane will not harm it. Some trace elements may reach the membrane. Their effect on the post-combustion CO_2 capture system is unknown.

Flue Gas Pretreatment Requirements – The flue gas desulfurization (FGD) system at EBS will remove SO_X, hydrogen chloride, soluble salts, and particulate matter (PM). EBS is also equipped with an electrostatic precipitator that will remove PM.

Membrane Replacement Requirements – Membrane modules will nominally be replaced every three years.

Waste Streams Generated – The post-combustion CO_2 capture system will generate liquid waste streams in the form of water condensate streams. Experience from test campaigns show that these streams are acidic and will either need to be pH-corrected prior to discharge or be combined and managed with other liquid waste streams present at the host power plant. Disposition and possible re-use of the condensates at EBS (e.g., as FGD makeup water) will be investigated as part of this design study. The current industry practice for membrane plants is to landfill the spent membrane elements. As part of the environment, health, and safety (EH&S) evaluation, the project team will review federal and state regulations regarding solid waste steams to determine if any flue gas contaminates entrained in the spent modules may require special handling or disposal. MTR's current understanding is that no special disposal measures are needed.

technology advantages

- The process does not use any hazardous chemicals. No new emission streams are produced.
- Reduces coal plant CO_2 emissions to those of a natural gas-fired plant.
- Utilizes MTR's second-generation Polaris™ membranes with CO_2 permeance two times that of their first-generation membrane technology.
- No modifications to existing plant steam cycle; potential to avoid NSR.
- Simple passive operation; no degradation caused by flue gas SO_X and NO_X.
- Compact modular system design.

R&D challenges

- Minimizing the cost of each tonne of CO_2 captured while maintaining current net output of the 600-MWe station.
- Efficiently supplying auxiliary power to the capture system at low cost.
- Upgrading the electrical interconnection to handle larger loads and avoid tripping the generator.

status

The project was completed, and a final report was delivered in September 2020. Four options for supplying power to the membrane system with a few variations therein were proposed and investigated, and a natural gas-powered simple-cycle configuration was selected as the option best suited for the study. An overall CO_2 capture rate of 52% (including emissions from the new GT system) was observed. The CO_2 system imposed an efficiency penalty of about 6.9 points (32.1% baseline to 25.2% with capture), resulting in a net cost of electricity increase of around $50–60/MW-hr (5–6 cents/kW-hr). Detailed results were made available in the final report.

available reports/technical papers/presentations

Dillon, D.," Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station Using Membrane-Based Technology," presented at the 2019 NETL Carbon Capture, Utilization, Storage and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/D-Dillon-EPRI-East-Bend-Membrane.pdf*.

Bhown, A., "Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station using Membrane-Based Technology," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

Dillon, D., "Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station using Membrane-Based Technology," Kick-off meeting presentation, Pittsburgh, PA, June 2018.

Dillon, D.; Chu, R.; Elliot, W.; Freeman, B.; McKaskle, R., "Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station Using Membrane-Based Technology," Final Project Report. Report Number: DOE-EPRI-31589. September 2020. *https://www.osti.gov/biblio/1686164*.

Large Pilot Testing of Linde-BASF Advanced Post-Combustion Carbon Dioxide Capture Technology at a Coal-Fired Power Plant

primary project goal

The University of Illinois is evaluating the design, construction, and operation of a 10 megawatt-electric (MWe) capture system based on the Linde-BASF advanced amine-based post-combustion capture technology at a coal-fired power plant. The project consists of three phases. Phase I was completed and consisted of a feasibility study that outlined preliminary engineering designs, conducted preliminary analysis of National Environmental Policy Act (NEPA)-related issues, and concluded selection of a host site for Phases II and III. Following Phase I, the project completed Phase II, which consisted of a detailed front-end engineering design (FEED) study, completing the NEPA Final Environmental Assessment (EA) with Finding of No Significant Impact (FONSI), and securing recipient cost-share commitments for Phase III. Phase III efforts are underway, consisting of detailed engineering, procurement of equipment and modules, construction and installation of the capture system, and operating test campaigns.

technical goals

Phase I objectives were to:

- Establish the feasibility of installing a 10-MWe capture facility at one of three potential pilot host sites.
- Select a host site based on the feasibility studies.
- Complete an Environmental Information Volume for each potential host site.
- Obtain necessary commitments from the selected site.
- Update the preliminary cost and schedule estimates provided in the Phase I proposal.
- Secure cost-share commitments for Phase II (Design) and develop a plan for securing cost-share commitments for Phase III (Construction/Operation).

Phase II objectives were to:

- Complete a FEED study for the proposed large-scale pilot, including a detailed cost and schedule estimate for Phase III for the installation of the 10-MWe pilot plant at the host site, followed by commissioning, start-up, operations, testing, and data collection for performance validation.
- Complete NEPA process at the host site.
- Draft permitting documentation to be submitted to appropriate authorities to initiate the permitting process and develop a clear understanding of timelines that will support Phase III.
- Document secured cost share for Phase III.
- Secure commitments for all necessary Phase III team members, including an engineering, procurement, and construction (EPC) firm to complete construction.

program area:

Point Source Carbon Capture

ending scale:

Large Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Linde-BASF CO_2 Capture Process for Coal-Fired Power Plants

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031581

Predecessor projects:

FE0026588
FE0007453

NETL project manager:

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partners:

Linde plc; Affiliated Construction Services; Affiliated Engineers Inc.; Visage Energy

start date:

04.04.2018

percent complete:

70%

- Update the techno-economic analysis (TEA) for the Linde-BASF technology integrated with a 550-MWe net supercritical pulverized coal power plant based on the most recent system design and cost information.

Phase III objectives are to:

- Complete construction of the 10-MWe capture system.
- Operate the system over the upcoming five years and compare the results with the 1.5-MWe testing at the National Carbon Capture Center (NCCC).
- Complete a full TEA for the upscaled plant.
- Perform a risk factor analysis.

technical content

The Linde-BASF advanced CO_2 capture process incorporating BASF's novel amine-based solvent, OASE® blue, with Linde's process and engineering innovations allows for a significant increase in energy efficiency and reduced cost for CO_2 recovery from coal-based power plants. In addition to a reduction in regeneration energy and a lower solvent circulation rate enabled by the BASF solvent, Linde has achieved significant improvements in process design, as shown in Figure 1, featuring an advanced stripper inter-stage heater design to optimize heat recovery in the process. This results in lower capital and operating costs for the CO_2 capture system. The Linde-BASF technology addresses all the major challenges for solvent-based carbon capture, including: (1) high specific energy for regeneration, (2) lack of stability due to thermal and oxidative degradation, (3) increased corrosiveness with increased CO_2 loading, and (4) lack of tolerance to impurities from coal combustion products. The design parameters for the solvent are shown in Table 1.

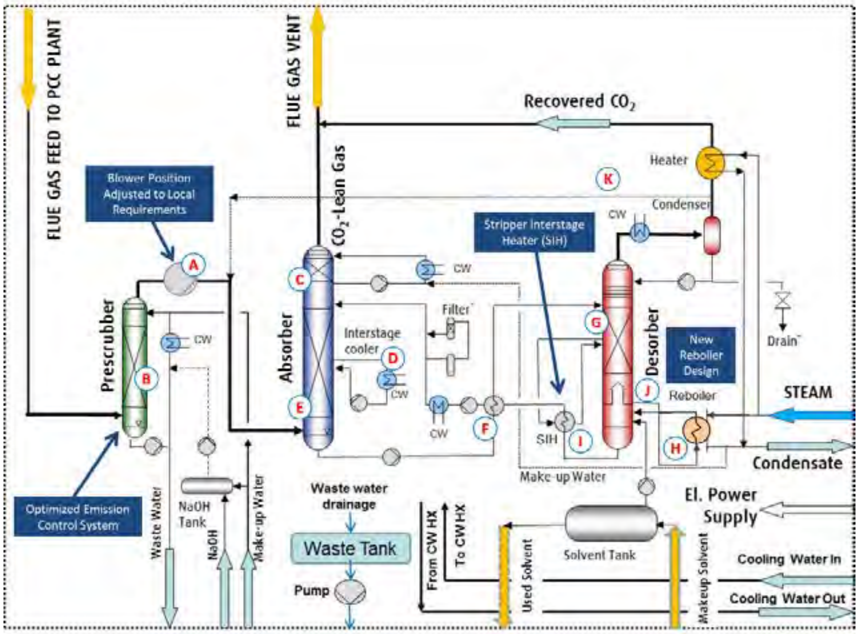

Figure 1: Large pilot process configuration for Linde-BASF technology with Highlighted design improvements.

A. Flue gas blower provides enough pressure to overcome the pressure drop across the pre-scrubber and absorber.

B. Integrated pre-scrubber and direct contact cooler to reduce SO_X content below 5 ppm and simultaneously cool the flue gas stream to ~35–40°C.

C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols.

D. A gravity-driven inter-stage cooler for the absorber that eliminates the pump and the controls.

E. High-capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction.

F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.

G. Regenerator designed for operation at pressures up to 3.4 bar(a), significantly reduces CO_2 compression energy and eliminates the bulky first stage of the CO_2 compressor train, resulting in capital cost savings.

H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to power plant load changes.

I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.

J. Variations of the stripper-reboiler flashing configuration, which are being evaluated for an ultimate reduction of solvent regeneration energy.

K. Optional CO_2 recycle stream, provided to evaluate the effect of plant loading and variable CO_2 concentration in the flue gas on overall energy consumption, and to limit the effects of power plant loading on flue gas CO_2 mol% fluctuations.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	proprietary	proprietary
Vapor Pressure @ 15°C	bar(a)	proprietary	proprietary

Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15°C/15°C)	—	proprietary	proprietary
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	proprietary	proprietary
Absorption			
Pressure	bar(a)	1.0	0.9-1.1
Temperature	°C	30-70	30-60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	proprietary	proprietary
Desorption			
Pressure	bar(a)	1.6-3.4	1.6-3.4
Temperature	°C	124-140	124-140
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary	proprietary
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	% / % / bar(a)	90%, 99.98% (dry), 3.4 bar(a)	90%, 99.98% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary	

Previous testing of a 0.45-MWe pilot plant incorporating the Linde-BASF technology and utilizing lignite-fired power plant flue gas has shown that the OASE blue solvent is stable, with little degradation observed over 55,000 hours, whereas the reference monoethanolamine (MEA) solvent started to degrade appreciably under the same conditions after 2,000 hours. The Linde-BASF CO_2 capture process was also previously tested at 1.5-MWe-scale at NCCC under project DE-FE0007453, supported by the U.S. Department of Energy (DOE). The study validated solvent stability and demonstrated a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact. This project leverages work done previously through a DOE Phase I grant (DE-FE0026588), in which a 15-MWe pilot plant of the Linde-BASF advanced CO_2 capture technology was designed to be integrated with the University of Illinois' Abbott Power Plant on the campus of the University of Illinois at Urbana-Champaign (UIUC), with the goal of capturing approximately 300 tonnes per day (tpd) of CO_2 at a 90% capture rate. The 15-MWe pilot project aimed to optimize the process at larger scale and gather performance data under realistic conditions to enable a robust commercial design. Phase I of the project resulted in the completion of a preliminary plant design with basic engineering and cost estimates; establishment of permitting needs; identification of approaches to address environmental, health, and safety concerns related to pilot plant installation and operation; and completion of a detailed TEA, demonstrating that the implementation of Phase II (Detailed Design, Construction, and Operation) of the project is feasible. The project also established strategies for workforce development for the operation and maintenance of carbon capture systems based on the Linde-BASF technology that are retrofitted to existing power plants.

The design and costing of the 10-MWe capture plant for installation at the selected host site (City Water, Light, and Power [CWLP] coal-fired power plant in Springfield, Illinois) was based on the estimate for the 15-MWe pilot in the previous DOE-funded project and established industry-scaling factors. The capture system will be installed in the Dallman 4 unit, which is a nominal 200-MWe pulverized coal-fired unit that became operational in 2009. The unit employs a Foster Wheeler front and rear wall-fired pulverized coal boiler equipped with low-nitrogen oxide (NO_X) burners; a selective catalytic reduction (SCR) unit for NO_X removal; a hydrated lime injection (HLI) system for sulfur trioxide (SO_3) removal; a fabric baghouse to capture particles; a flue gas desulfurization (FGD) system to mitigate sulfur dioxide (SO_2) emissions; and a wet electrostatic precipitator (ESP) to remove liquid droplets, such as sulfuric acid mist. For the 10-MWe capture pilot, a slipstream of flue gas from the Dallman 4 unit will be utilized as a feed gas for CO_2 capture.

Based on results from small pilot studies and the TEA, the technology will achieve high CO_2 capture (≥90%) and generate high-purity (>99.9%) captured CO_2 in a cost-effective manner. TEA results indicated that when the proposed advanced Linde-BASF technology is integrated with a 650-MWe net supercritical pulverized coal power plant, there will be an increase in power plant efficiency of approximately 1.2 percentage points, a nominal 12.6% reduction in COE, and 26.3% reduction in cost of CO_2 capture ($/MT) compared to the latest DOE/National Energy Technology Laboratory (NETL) base case (Case B12B reference). A summary of the expected economics results is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/megatonne CO_2	$55.60	$41.01
Cost of Carbon Avoided	$/megatonne CO_2	n/a	n/a
Capital Expenditures	$/MWhr	$50.98	$40.18
Operating Expenditures	$/MWhr	$54.24	$50.70
Cost of Electricity	$/MWhr	$114.12	$99.78

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero, i.e., not taking into account atmospheric pressure.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		mol%					ppmv	
psig	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
0	135	9.8	17	67	5.3	0.80	34	30

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbon dioxide in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operation, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 parts per million (ppm) in order to limit solvent degradation and is implemented in a direct contact cooler in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE Blue solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the direct contact cooler where SO_X and NO_X are removed; this stream will go through an oxygenation treatment that converts sulfite and bisulfite compounds into sulfate compounds prior to being discharged to the local sanitary district. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – See Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

technology advantages

- Significant reduction in specific regeneration steam consumption (24–40% lower), electrical power (14–26% lower), and cooling water duty (32–43% lower) compared to a reference MEA plant.
- Increased higher heating value efficiency (HHV) for power production (up to ~32.7% efficiency) and lower thermal load compared to a reference MEA plant (28.4% efficiency) due to a combination of advanced solvent and process improvements, including integrated pre-scrubber and direct contact cooler, downstream gas blower, higher desorber pressure, and interstage gravity-flow cooler.
- The total plant costs are ~20% lower compared to a reference MEA plant, with significantly lower post-combustion capture plant capital costs.
- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is the producer of the OASE Blue solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.

- The Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant EPC, commercial deployment, and long-term, continuous operations.

R&D challenges

- Scale-up of absorber column at low cost, maintaining uniform vapor and liquid distribution.
- Optimizing operation of the stripper to reduce steam utilization and increase energy efficiency of the CO_2 capture process using advanced stripper configurations and stripper inter-stage heating.
- Managing flue gas impurities and aerosol formation to reduce amine losses.
- Testing of new process units for energy optimization.
- Integration with operations at the CWLP host site.

status

In Phase I, the CWLP coal-fired power plant in Springfield, Illinois, was selected as the host site for the large pilot (10 MWe) capture plant and Phase II cost-share commitments were finalized. Preliminary engineering and cost estimates were prepared for the equipment inside the battery limit (ISBL) and outside the battery limit (OSBL). A NEPA contractor, ICF International Inc., was also selected as part of the Phase I effort. A plan was developed for securing cost-share commitments for Phase III.

In Phase II, a detailed FEED study was performed and completed, including equipment cost estimates. All required NEPA/permitting issues have been resolved and cost-sharing estimates have been finalized.

Phase III is currently underway and is set to conclude in 2026.

available reports/technical papers/presentations

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[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Engineering-Scale Testing of Transformational Non-Aqueous Solvent-Based Carbon Dioxide Capture Process at Technology Centre Mongstad

primary project goal

Research Triangle Institute (RTI) is developing and testing, at large pilot scale, a non-aqueous solvent (NAS; i.e., water-lean solvent) carbon dioxide (CO_2) capture process to confirm the potential to reduce the parasitic energy penalty associated with the capture of CO_2 from flue gas; demonstrate the long-term process operational reliability at static and dynamic conditions; and verify the solvent degradation rate, emissions, solvent loss, and corrosion characteristics of the solvent at engineering scale.

technical goals

- Evaluate water-lean solvent degradation and material compatibility.
- Measure water-lean solvent performance over static and dynamic operating conditions.
- Design/procure water-lean solvent-specific components for implementation in the host site facility.
- Confirm a reduction in parasitic energy penalty to less than 2.6 gigajoules (GJ)/tonne CO_2 captured.
- Complete a techno-economic analysis (TEA) to confirm RTI's NAS process can reduce CO_2 capture costs.

technical content

RTI is advancing the development of a water-lean solvent-based CO_2 capture process that was previously developed and tested at lab- and bench-scale (~10 kilowatts [kW]) with simulated flue gas under the U.S. Department of Energy (DOE)-funded project FE0013865. Water-lean solvents have the potential to significantly reduce the cost of CO_2 capture from coal-fired flue gas when compared to aqueous amine-based solvent processes by reducing the energy required for solvent regeneration. RTI's water-lean solvent is a hydrophobic, sterically hindered, carbamate-forming amine with low-water solubility solubilized in a diluent having low vapor pressure and low viscosity. It is characterized by low heats of absorption and generation of high CO_2 partial pressures at low temperatures and has the potential to reduce the regeneration energy to less than 2.1 GJ/tonne CO_2. The overall reboiler heat duty, or thermal regeneration energy, is made up of the sensible heat, heat of vaporization of water, and heat of absorption. The heat of vaporization, due to the lack of water, is significantly less for water-lean solvents than for aqueous amine-based processes. Also, water-lean solvents overcome the foaming issues that are often associated with aqueous

program area:
Point Source Carbon Capture

ending scale:
Large Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent for Coal-Fired Flue Gas

participant:
Research Triangle Institute

project number:
FE0031590

predecessor projects:
FE0026466
FE0013865

NETL project manager:
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principal investigator:
Marty Lail
Research Triangle Institute
mlail@rti.org

partners:
Technology Centre Mongstad (TCM); Electric Power Research Institute Inc.

start date:
08.08.2018

percent complete:
82%

solvents, as shown in Figure 1. RTI's CO_2-rich water-lean solvent has a viscosity of less than 30 cP and is non-foaming.

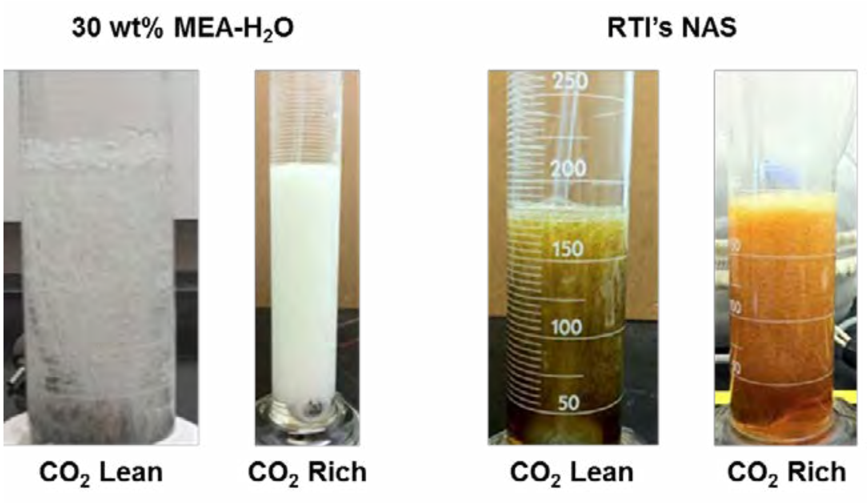


Figure 1: Comparison of foaming in aqueous and RTI's water-lean solvents.

The NAS CO_2 capture process includes a solvent regenerator design specifically for water-lean solvents that combines heat delivery and gas release in a single-step process unit to maintain lower regeneration temperatures. The process, as shown in Figure 2, is like conventional solvent scrubbing systems with key novel design features:

- NAS solvent recovery and wash section—similar to water washing, but water-lean solvents have low water-solubility.
- Solvent regenerator—lack of low-boiling component (conventional reboilers are not applicable).

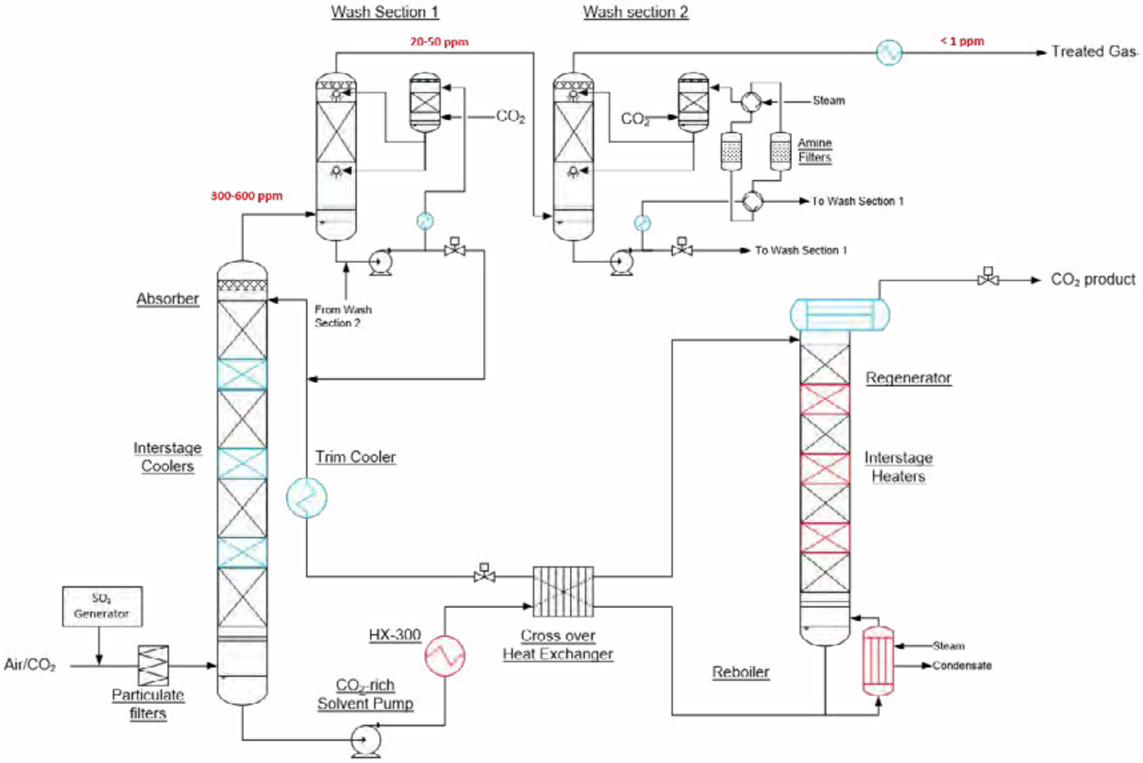
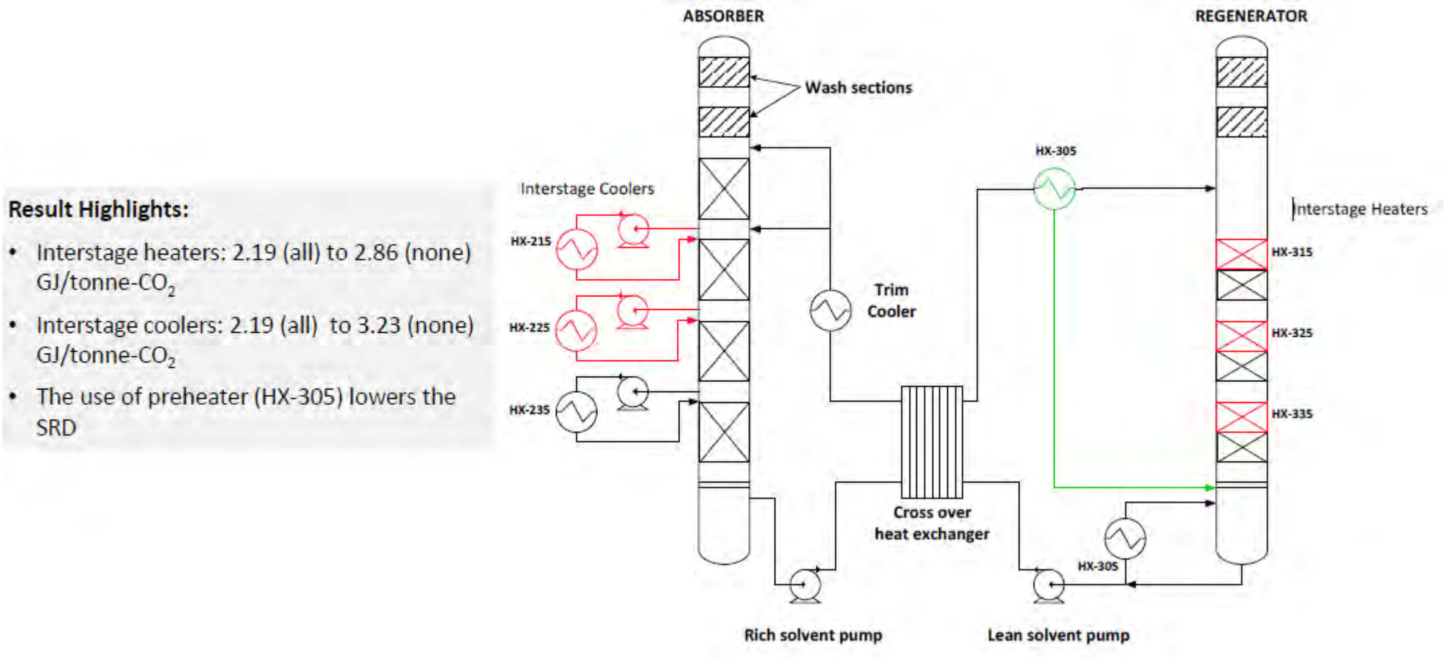


Figure 2: NAS CO_2 capture process diagram.

Under DOE-funded project DE-FE0026466, RTI used the bench-scale test unit (up to 60 kW) at SINTEF's Tiller plant to experimentally show that the water-lean solvent can achieve 90% CO_2 capture and generating a high-purity CO_2 product (greater than 95% CO_2), as well as to evaluate the effectiveness of the developed NAS recovery/wash section and solvent regenerator design. Bench-scale testing at SINTEF's Tiller plant was first performed using the monoethanolamine (MEA) control and the water-lean solvent in an unmodified configuration of the test unit. Baseline testing of the water-lean solvent using propane and coal-fired flue gas was performed over a period of approximately four months, showing a CO_2 capture rate of approximately 90%. Heat stable salts (HSS) and metals analyses were used to determine the solvent stability and corrosion. The HSS level was relatively constant and low during the test campaign. The results also indicate that the corrosion rate of NAS is quite low and stable, confirming previous test results that showed much lower corrosion rate for NAS as compared with MEA.

As the CO_2 capture system at Tiller was designed specifically to achieve the optimum performance for an aqueous-based solvent, it is not an ideal setup to realize the energy reduction benefit by using the water-lean solvent. Based on the knowledge acquired throughout the testing in RTI's gas absorption system (BsGAS) with various process configurations, the following modifications (Figure 3) to the existing absorption system at the Tiller plant were made:

- Addition of two interstage coolers between existing sections of packing in the absorber.
- Replacement of three existing packing sections in the regenerator column with three new sections consisting of an electric/steam heating portion located at the top-half of the section and a high surface area packing portion located at the bottom-half of the section.
- Expansion of lean-rich heat exchanger by adding a second crossover plate-and-frame heat exchanger in series.
- Addition of coal-fired burner.
- Rich solvent preheater installed at regenerator inlet.
- Addition of an acid wash/water wash section.



Result Highlights:

- Interstage heaters: 2.19 (all) to 2.86 (none) GJ/tonne-CO_2
- Interstage coolers: 2.19 (all) to 3.23 (none) GJ/tonne-CO_2
- The use of preheater (HX-305) lowers the SRD

Figure 3: Design improvements for NAS-based process.

The solvent formulation was also refined to increase CO_2 loading and working capacity and to reduce the reboiler heat duty required for solvent regeneration. The improved formulation (NAS-5) results in an increase in CO_2 working capacity from ~0.45 mol_{CO2}/mol_{amine} to ~0.48 mol_{CO2}/mol_{amine}, a decrease in heat of absorption from ~82 kilojoules (kJ)/mol_{CO2} to ~75 kJ/mol_{CO2}, and is expected to reduce the reboiler heat duty by decreasing the liquid/gas (L/G) ratios and the heat of absorption at higher temperatures. Through testing in RTI's bench-scale BsGAS, it was found to be advantageous to use two interstage coolers in the absorber column (with one at the bottom and one at the top) to achieve a heat duty near 2 MJ/kg-CO_2. The coolers play an essential role in lowering the temperature in the absorber column to maintain a high CO_2 loading in the solvent. A wash column was added to RTI's BsGAS to allow for testing different conditions to reduce amine losses for the technology, demonstrating that the wash section could effectively remove 92–93% of the amine emissions from the absorber. The process parameters of the solvent are shown in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	$/kg	14	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38
Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/kg CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28
Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45–1.13*	0.45
Heat of Desorption	kJ/kg CO_2	2,100*	2,045

* Experimentally measured data.

** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Following the installation of the NAS-specific components into the Tiller plant, including a new particulate filter, updated coal-burner control software, additional absorber intercoolers, additional water wash section, regenerative “inter-heaters,” and one additional crossflow heat exchanger, parametric testing was performed with NAS-5 to allow optimal operating conditions to be identified and long-term testing to be completed. Test results showed an average CO_2 capture rate of 90% and the lowest reboiler heat duty obtained was 2.3 GJ/tonne CO_2 when the rich solvent pre-heater was used.

Additional baseline testing of the new water-lean solvent formulation was performed at the National Carbon Capture Center (NCCC) to investigate solvent degradation, corrosion, and emissions using the Slipstream Solvent Test Unit (SSTU) with long-term exposure to coal-derived flue gas from the Gaston Power Plant in Wilsonville, Alabama. The NCCC system was operated for 580 hours with flue gas with intermittent delays. The effects of flue gas velocity, CO_2 capture efficiency, and aerosols on amine emissions were studied during the test campaign. Preliminary testing has indicated that the water-lean solvent displays minimal corrosion; therefore, the materials of construction for some of the equipment could be replaced with lower cost options. A TEA and environmental, health, and safety (EH&S) assessment of the NAS process based on test data obtained from SINTEF’s Tiller plant and from the SSTU at NCCC show that the NAS technology has the potential to meet DOE’s $40/tonne CO_2 capture target when it is fully developed and poses little EH&S risk.

In RTI’s current DOE-funded project, engineering-scale tests are being performed using the existing large pilot infrastructure at the Technology Centre Mongstad (TCM) in Norway. The test campaign includes baseline testing with the water-lean solvent in TCM’s 12-megawatt-electric (MWe) pilot plant in the configuration designed for aqueous-amine solvents, a hardware revamp of the plant to implement NAS-specific components, and follow-on NAS testing under optimized conditions. Based on the findings realized during the evaluation of RTI’s BsGAS and SINTEF’s Tiller plant under various process configurations, the following modifications to the existing system at TCM are being made:

- Addition of one interstage cooler between existing sections of packing in the absorber.
- Higher capacity pump in the thermosyphon reboiler for efficient regeneration.

- Adjustment of water wash flue gas inlet to maintain volume during operation.

In addition, strategies for reducing the amine emissions to less than 1 part per million (ppm) are being implemented to meet TCM's emissions requirements, including modifying the existing water wash section of the TCM unit, lowering the gas flow rate, and adding an intercooler to the absorber. Large pilot-scale test results will be used to demonstrate the applicability of the water-lean solvent as a drop-in replacement solvent in conventional capture systems and the process scalability and commercial potential of RTI's transformational NAS CO_2 capture process for pulverized coal power plants.

Included in this study is a TEA. The economic data for the current integrated power plant with CO_2 capture is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	43.3	43.3
Cost of Carbon Avoided	$/tonne CO_2	59.2	59.2
Capital Expenditures	$/MWhr	62.4	62.4
Operating Expenditures	$/MWhr	25.7	25.7
Cost of Electricity	$/MWhr	80.95	80.95

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxides (SO_X) and nitrogen oxides (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2–0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

technology advantages

- Low water solubility.
- Reduced regeneration energy.
- High solvent regeneration pressure at low regeneration temperatures, such that desorbed CO_2 can go directly to second stage of compression.
- Favorable thermodynamics.
  - Low heat of absorption.
  - High working capacity based on vapor-liquid equilibrium (VLE).
- Excellent thermal and oxidative stability; no formation of HSS.
- Low vapor pressure (less than 0.3 kPa [40°C], less than 10 ppm emissions in treated flue gas).
- Low conductivity; low corrosion rates.
- Low oxygen solubility.

R&D challenges

- Implementation of NAS-specific components into host site facility.
- Effective control of water content in both the rich and lean water-lean solvent solution to minimize regeneration energy required.
- Minimizing the rise in absorber temperature.
- Operating TCM plant within emissions requirements.
- Obtaining sufficient heat exchange for optimal performance.
- Improving the working capacity of the solvent.
- Solvent emissions control.

status

RTI has tested multiple water-lean solvent formulations and identified an improved formulation (NAS-5). Experimental testing of NAS-5 in RTI's BsGAS showed that the lowest regeneration of 2.15 MJ/kg CO_2 was achieved when the system operated at L/G of 4.2. The team performed 405 hours of NAS baseline testing at the SINTEF Tiller plant in an unmodified configuration, revealing that the energy required for solvent regeneration is 15% lower for NAS than that for MEA, even though NAS was run under less-than-optimal conditions. Parametric testing and a cumulative 1,200 hours of long-term testing of NAS-5 in the Tiller plant were conducted following installation of NAS-specific components to determine optimal operating parameters and validate reduced reboiler duty. The lowest specific reboiler heat duty of 2.3 GJ/tonne CO_2, water balance, and operational stability were maintained during about 1,600 hours of testing using the NAS-5 formulation. Additional water-lean solvent baseline testing using coal-fired flue gas at NCCC showed that 90% CO_2 capture is consistently observed under varying test conditions. In preparation for large pilot-scale testing, RTI initiated design and engineering of TCM facility modifications, as well as a front-end engineering design (FEED) study to determine the cost of modifications. In addition, solvent qualification testing was completed at SINTEF to demonstrate performance of the manufactured solvent. RTI has received and installed the key components for the facility modifications (interstage cooler, recirculation pump, etc.) to begin commissioning as of February 2022.

available reports/technical papers/presentations

Lail, M., 2021, "Engineering Scale Testing of Transformational Non-Aqueous Solvent-Based CO_2 Capture Process at Technology Center Mongstad." Presented at the 2021 Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lail.pdf*.

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Zhou, S. James, et.al., 2018, "Pilot Testing of a Non-Aqueous Solvent (NAS) CO_2 Capture Process," 14th International Conference on Greenhouse Gas Control Technologies, GHGT-14, 21st -25th October 2018, Melbourne, Australia.

Zhou, S. James et al., 2018, "Engineering Scale Testing of Transformational Non-Aqueous Solvent-Based CO_2 Capture Process at Technology Centre Mongstad," Project Kickoff Meeting, October 2018. *https://netl.doe.gov/projects/plp-download.aspx?id=10417&filename=Engineering+Scale+Testing+of+Transformational+Non-Aqueous+Solvent-Based+CO2+Capture+Process+at+Technology+Centre+Mongstad.pdf*.

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Tanthana, J., 2018, "Large Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Tanthana-RTI-Non-Aqueous-Solvent-Capture-Process.pdf.*

Zhou, S., 2017, "Large Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants Utilizing Real Coal Derived Flue Gas," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/S-J-Zhou-RTI-Non-Aqueous-Solvent-CO2-Capture.pdf*.

Zhou, S. James, et. al., 2017, "Large Bench-scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-fired Power Plants," 9th Trondheim Conference on CO_2 Capture, Transport and Storage, Trondheim, Norway, June 12 - 14, 2017.

Zhou, S., 2017, "Large Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants Utilizing Real Coal Derived Flue Gas," Budget Period 1 Project Review Meeting, Pittsburgh, PA, April 2017.

Lail, M., 2016, "Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants," Final Scientific/Technical Report, December 2016. *https://www.osti.gov/servlets/purl/1389565*.

Zhou, S. James, et. al., 2016, "Non-Aqueous Solvent CO_2 Capture Process," *Proceedings of the 13th Annual International Conference on Greenhouse Gas Control Technologies.* Lausanne, Switzerland. November 14 - 18

Lail, M., 2016, "Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants," 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *http://netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/M-Lail-RTI-Non-Aqueous-Solvent-CO2-Capture.pdf*.

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Coleman, L., 2014, "Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process

primary project goal

Membrane Technology and Research Inc. (MTR) is advancing their innovative membrane-based post-combustion carbon dioxide (CO_2) capture process to the pre-commercial stage of development. The goal of this three-phase project is to design, build, and operate a 150-tonne-per-day (TPD) large pilot capture system at the Wyoming Integrated Test Center (WITC) in Gillette, Wyoming. The membrane large pilot is designed to achieve approximately 70% CO_2 capture from a 10-megawatt-electric (MWe) equivalent slipstream of flue gas. This range of partial capture using membranes offers the lowest cost of capture (\$/tonne CO_2). Phases I and II have been completed. Completion of all phases of this project will signify that the MTR membrane capture process is ready to proceed to the demonstration scale.

technical goals

Phase I (Year 1) objectives were to:

- Select a host site and secure cost-share commitments from the selected site.
- Conduct an initial Environmental Information Volume (EIV) and preliminary National Environmental Policy Act (NEPA) review of the test unit at the host site.
- Complete a preliminary design of the pilot system and obtain budgetary estimates from vendors.
- Finalize team commitments and organization for subsequent phases.

Phase II (Year 2) objectives were to:

- Complete required permit processes at the host site.
- Complete an EIV and NEPA review.
- Complete a front-end engineering design (FEED) study and update budgetary estimates and schedule for Phase III.
- Complete an updated techno-economic analysis (TEA) of the process based on the most recent system design and cost information.
- Secure host site and cost-share commitments for Phase III.

Phase III objectives are to:

- Complete construction of the 150-TPD membrane system.
- Install and operate the large pilot system at the host site.

technical content

MTR has developed a new class of membranes, called Polaris™, that have 10 times the CO_2 permeance of conventional gas separation membranes. A tenfold increase in permeance leads to a tenfold decrease in the required membrane area, which substantially reduces the capital cost and footprint of the capture system. These membranes, along with innovative process modifications, address challenges for post-combustion carbon capture.

program area:
Point Source Carbon Capture

ending scale:
Large Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Large Pilot Testing of Polymer Membrane System

participant:
Membrane Technology and Research, Inc.

project number:
FE0031587

predecessor projects:
FE0026414; FE0007553; FE0005795

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partners:
The Wyoming Integrated Test Center; Sargent & Lundy; Trimeric Corporation; Electric Power Research Institute

start date:
04.01.2018

percent complete:
55%

Over the past decade, MTR has worked with the U.S. Department of Energy (DOE) to develop these innovations into a cost-effective CO_2 capture process. As a result of these successes, the technology was scaled-up to a 20-TPD (1-MWe) small pilot system that was operated in slipstream tests at the National Carbon Capture Center (NCCC). These activities have brought the MTR technology to the point where it is ready for large pilot evaluation. The large pilot system to be built in this project will be based on the fully validated Gen-1 Polaris membranes. This membrane has been scaled-up to commercial production quantities. In addition to successful use for CO_2 capture in field tests at the NCCC and Babcock & Wilcox Enterprises Inc. (B&W), the Polaris Gen-1 membrane has been used in commercial natural gas and refinery membrane applications.

A simplified version of the process to be used in the pilot plant is shown in the block diagram in Figure 1.

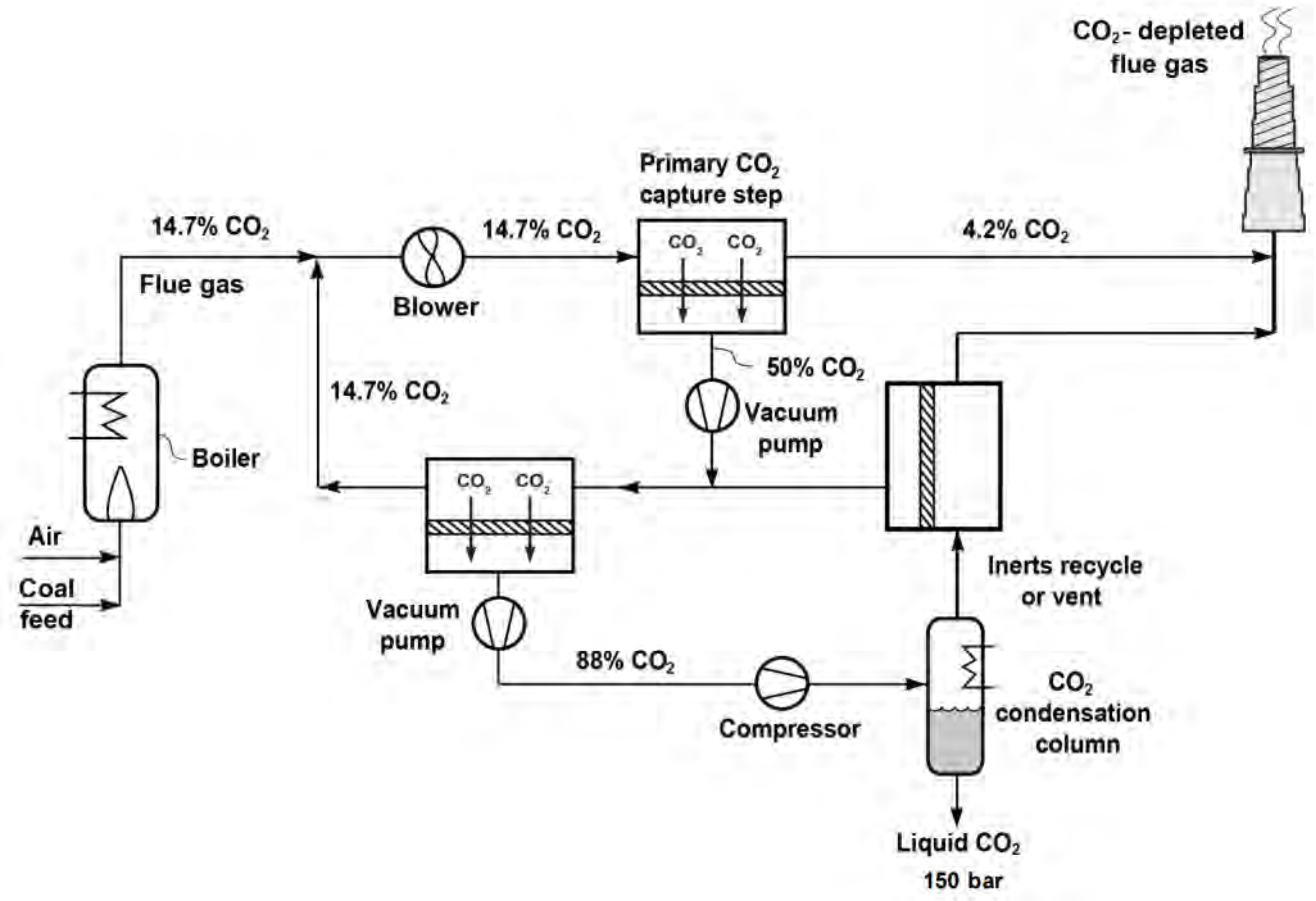

Figure 1: Simplified block diagram of the MTR large pilot CO_2 capture plant to be built.

The large pilot unit will capture approximately 70% of the CO_2 content (150 TPD) from a 10-MWe slipstream of flue gas provided by WITC. The flue gas to be delivered to the unit is at 85°C and contains 12.7% CO_2 and 18% water on average. A blower is used to increase the flue gas pressure to 1.2 bar absolute. The flue gas is then cooled in a direct contact cooler (DCC). A dedicated evaporative cooling tower will produce the cooling water required for the DCC and the various vacuum and compression intercoolers and aftercoolers. The DCC reduces the water content of the gas to 1.5% and increases the CO_2 content to approximately 15%.

The gas leaving the DCC then enters the first-stage membrane modules. The membranes partition the gas into a CO_2-enriched permeate (~50% CO_2) and a CO_2-depleted vent gas (~4% CO_2). The CO_2-depleted flue gas is vented to the atmosphere via a dedicated stack.

The driving force for CO_2 permeation is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. From the discharge of the vacuum pump, the CO_2-enriched permeate is compressed to about 1.1 bar and sent to a second-stage membrane, which further enriches the gas to approximately 85% CO_2. The second-stage membrane unit is much smaller than the first one and uses a vacuum pump to provide driving force.

The twice enriched permeate gas from the second membrane stage is compressed to 25 bar. Some of the water in the gas is removed in the inter-stage cooler of the compressor. Most of the water that remains is removed from the compressed gas by cooling to 5°C. A molecular sieve drier is then used to produce bone-dry gas. The dry gas is passed to a low-temperature distillation unit to provide high-purity CO_2. The liquid CO_2 is then pumped to 153 bar as required for enhanced oil recovery (EOR) or storage.

A model of the 150-TPD large pilot membrane skid is shown in Figure 2. The membranes are housed in low-pressure-drop modules, which reduce cost and increase packing density. There are eight modules per stack and six stacks per container skid. The skids are stacked two high, with a total of six containers for the large pilot (five skids for first-stage membrane separation and one skid for second-stage membrane separation). This will be the final form factor for this membrane CO_2 capture technology. The membrane portion of the capture plant has a compact footprint, processing 10 MWe of flue gas in an area of approximately 100 by 100 feet, with a maximum height of 30 feet.

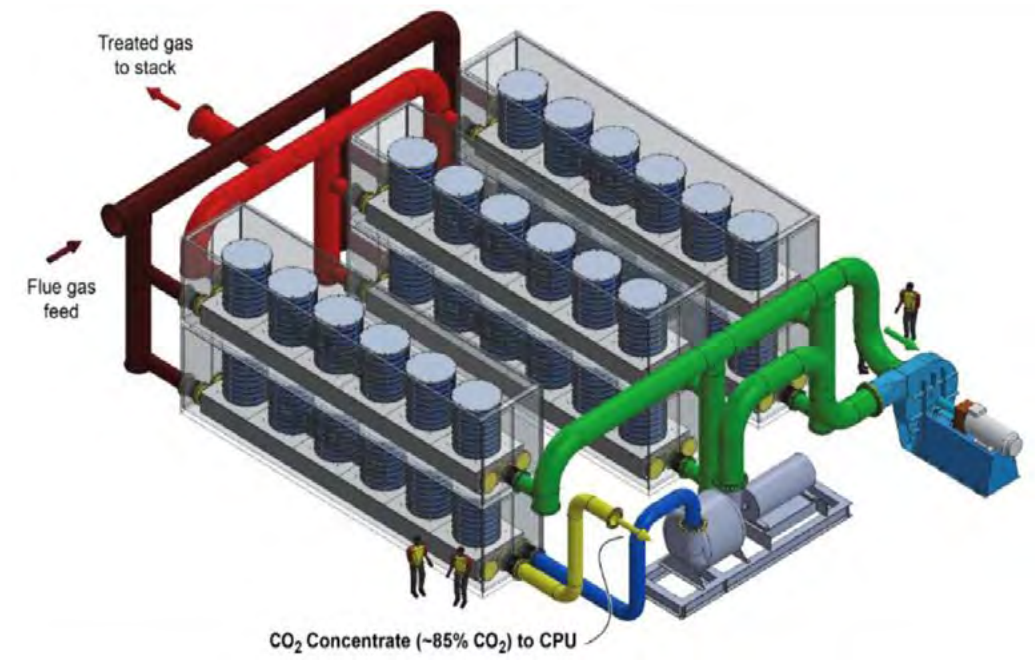

Figure 2: Preliminary general arrangement drawing of the 150-TPD large pilot system to be installed at WITC.

WITC will provide the test site and a significant cost-share contribution for the Phase II and Phase III programs. WITC is located in Gillette, Wyoming, adjacent to the Basin Electric Dry Fork 420-MWe coal power plant. Basin Electric will supply the project with the equivalent of 10 MWe of flue gas. Duct work and fans to deliver flue gas to the test site are in place. Power and water necessary for the project have also been installed. The membrane unit will recover approximately 70% of the CO_2 content of this gas, or approximately 150 TPD. At full-scale, a 70% reduction in CO_2 emissions would bring the remaining CO_2 emissions of a coal power plant to below that of an equivalent-sized natural gas power plant.

All the objectives of the Phase I feasibility study were met. Preliminary engineering drawings for the 150-TPD plant have been prepared. Budget estimates have been obtained for the major equipment items and initial cost estimates for the Phase III construction and operation work have been prepared. A preliminary cost analysis indicates that at the end of the Phase III program, the technology will be ready for scale-up to large demonstrations and CO_2 capture costs in the $40/tonne CO_2 range will be possible.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	11,000 h	11,000 h
Manufacturing Cost for Membrane Material (Module and Skid)	\$/m^2	50-100	50-100
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000	2,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	flue gas	flue gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	tons/hr	70.31	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-75%, 99%, 153 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.05/sweep: 0.025	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation occurs by a passive, solution-diffusion process. Permeation driving force through the first-stage membrane module is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, etc., is unknown.

Flue Gas Pretreatment Requirements – Testing at the NCCC showed no additional pretreatment was required downstream of a wet flue gas desulfurization (FGD).

Membrane Replacement Requirements – Greater than three-year membrane lifetime.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

technology advantages

- The process does not use any hazardous chemicals. No new emission streams are produced.
- The membranes developed are 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The system is compact and modular.
- The two-stage membrane design allows for high-purity CO_2 combined with high capture rates.
- The low-pressure-drop modules reduce parasitic energy.
- The system is very efficient at partial capture (50 to ~70%).

R&D challenges

- There is a risk that the membranes may be less stable at large scale than anticipated.

status

MTR successfully completed all Phase I and Phase II activities, including an EIV, FEED, and NEPA documentation for the construction and large pilot testing of the MTR membrane post-combustion CO_2 capture process. The environmental permit for construction was obtained from the Wyoming Department of Environmental Quality. MTR finalized the engineering and design documentation and developed near-final contract and financial commitment documents for execution in Phase III. The results of the constructability review in Phase II will be used for procuring the equipment and services for the construction of the large pilot unit in Phase III. The overall design of the 150-TPD large pilot plant was finalized. Preliminary layout drawings for the system at the WITC site were prepared. In addition, MTR completed the design and purchased equipment for the fabrication of the planar module test station to perform performance and leak testing of fabricated modules. The Phase III project team was assembled and a division of responsibilities for the Phase III program was completed, along with an updated schedule and budget.

available reports/technical papers/presentations

Baker, R.W., et al. "Phase III: Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process," presented at the 2021 Carbon Management and Oil and Gas Research Project Review Meeting - Point Source Capture - Lab, Bench, and Pilot-Scale Research, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Baker.pdf.*

Baker, R.W., et al. "Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process," presented at the 2020 NETL Integrated Project Review Meeting - CCUS Integrated Projects, August 2020. *https://netl.doe.gov/sites/default/files/netl-file/20CCUS_Baker.pdf*.

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Baker, R.W., et al. “Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/R-Baker-MTR-Membrane-Testing%20r1.pdf*.

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Baker, R.W., et al. “Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process,” Phase I kickoff meeting presentation, Pittsburgh, PA, May 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10402&filename=Large+Pilot+Testing+of+the+MTR+Membrane+Post-Combustion+CO2+Capture+Process.pdf*.

Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology

primary project goal

Membrane Technology and Research Inc. (MTR) will design, build, and operate an advanced Polaris™ membrane carbon dioxide (CO_2) capture system at the Technology Centre Mongstad (TCM) using actual flue gas from a refinery catalytic cracker, which simulates coal flue gas. This test system will validate recent membrane technology advancements and mitigate risk in future scale-up activities. The overall MTR membrane process will show the potential to meet the 2030 U.S. Department of Energy (DOE) target of $30/tonne CO_2 captured from coal-fired power plants. This project will demonstrate a cost-effective advanced membrane process to capture CO_2 from flue gas through slipstream tests at TCM using commercial-scale components. Results from this field test will provide performance data to allow a thorough technical and economic evaluation of the proposed membrane process. Successful completion of this project will signify readiness to proceed to the next step—testing a larger proof-of-concept advanced membrane system on the scale of 10–25 megawatts-electric (MWe).

technical goals

- Design the membrane test system and complete host site preparations.
- Fabricate commercial-scale membranes and low-pressure-drop membrane modules.
- Fabricate membrane test system skid, with membrane modules incorporated into skid, and install system at TCM.
- Conduct a minimum six-month field test, including three months of steady-state operation and parametric tests that focus on verifying system performance at partial capture rates that minimize capture costs.
- Evaluate optimal integration of advanced compression into the membrane capture process, including cost estimates.
- Complete a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment of the membrane capture technology.

technical content

In this project, no additional membrane development is required. A previously validated second-generation (Gen-2) membrane will be scaled-up to commercial manufacturing equipment. It is expected that this production scale-up process will produce cost savings through bulk materials usage and application of automated manufacturing equipment.

The goal of this project is to scale-up advanced Polaris Gen-2 membranes and modules to a final form optimized for commercial use, and to validate their transformational potential in an engineering-scale field test at TCM. This program will expand on work conducted by MTR over the past decade with DOE support to develop efficient membrane CO_2 capture technology. This effort has produced the MTR Polaris class of membranes and a patented selective recycle process design that lowers the cost of capture.

program area:

Point Source Carbon Capture

ending scale:

Large Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Polymeric Membranes for Coal-Fired Power Plants

participant:

Membrane Technology and Research, Inc.

project number:

FE0031591

predecessor projects:

FE0005795
FE0026414

NETL project manager:

Andrew O'Palko
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principal investigator:

Tim Merkel
Membrane Technology and Research Inc.
tim.merkel@mtrinc.com

partners:

Technology Centre Mongstad; Dresser-Rand; Trimeric Corporation; WorleyParsons/Advisian

start date:

08.01.2018

percent complete:

80%

Over the course of this development effort, key improvements made included higher-permeance membranes, low-pressure-drop modules, and a process design that optimizes the efficiency of capture.

The Polaris Gen-2 membranes have demonstrated 70% higher CO_2 removal capacity compared to the original membrane in bench-scale tests at the National Carbon Capture Center (NCCC) (Figure 1). They will be packaged into new modules designed for low-pressure flue gas treatment. Prototypes of these modules have been validated in prior field trials that confirm large energy and cost savings. Assemblies of these modules will be fitted into a standard container that represents the final form factor for this technology, with future commercial systems simply utilizing large numbers of this modular repeat unit.

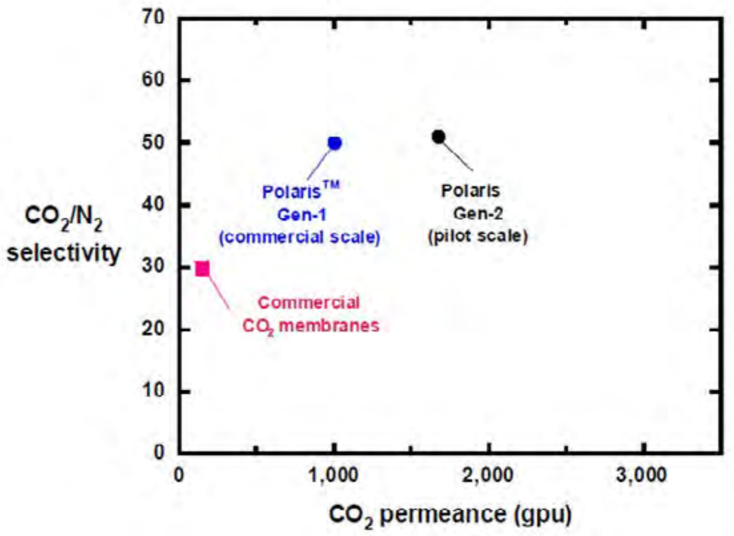

Figure 1: A CO_2/N_2 trade-off plot showing data for two generations of MTR Polaris membrane. Data are pure-gas values at room temperature.

These step-change material and device advances will be incorporated into a system design that takes advantage of the inherent efficiency of membranes for bulk separations. Capture costs can be minimized by operating at partial capture rates (50–80%), while still reducing coal plant CO_2 emissions to that of a gas-fired power plant or less. Finally, the pairing of Polaris Gen-2 membrane technology with advanced compression technology will be investigated. This technology combination was previously featured in the DOE Pathways Study as an attractive way to reach future cost targets.

In addition to an advanced membrane material, this project will also utilize a new type of low-pressure-drop module. This plate-and-frame module, in addition to its relatively compact size, had about four times lower pressure-drop as prior spiral modules during field testing at NCCC under the same conditions (Figure 2), resulting in large energy savings.

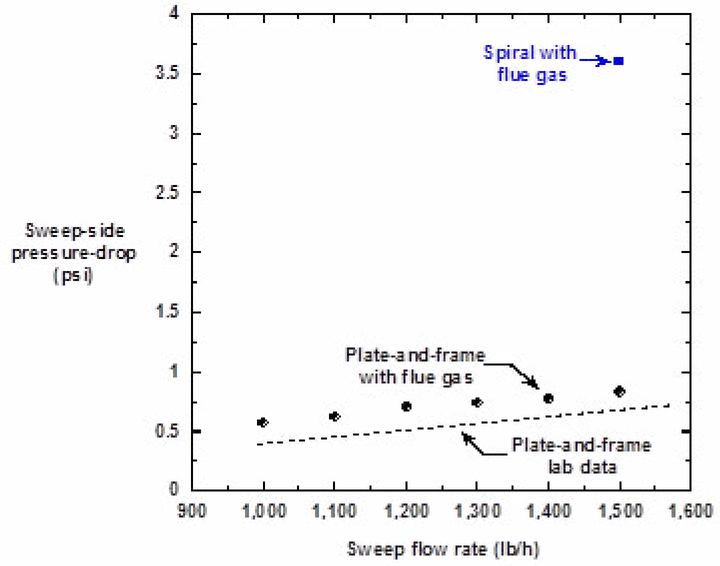

Figure 2: Difference in pressure-drop between spiral and plate-and-frame modules in NCCC field tests.

To reduce the cost of the membrane modules, MTR plans to fabricate them from structural plastics. During this project, a mold flow analysis was completed for the new module design. With this analysis, any issues with the mold design can be identified prior to actual fabrication of the mold and the molding company can determine how to operate their machinery with the MTR mold. Various process parameters were profiled and optimized, including temperature, pressure, number of gates, and gate locations.

Using the mold flow analysis, MTR, along with the domestic mold fabricator and custom plastics injection molding companies, finalized a mold design. A detailed drawing of the new planar stack containing eight membrane modules is shown in Figure 3. The process parameters for these membranes are shown in Table 1.

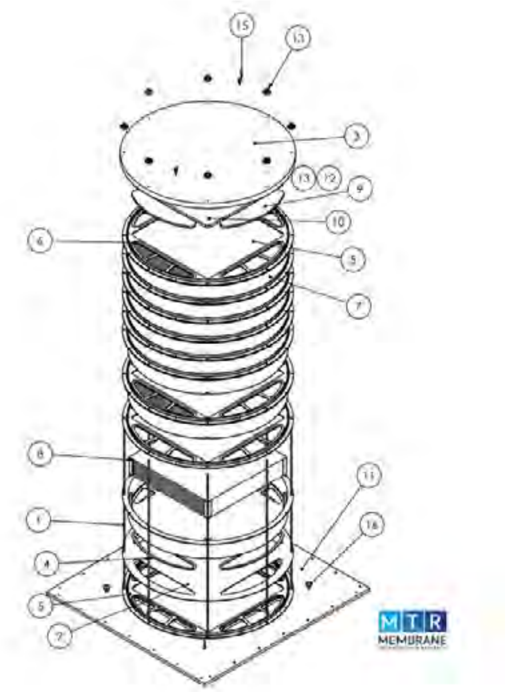

Figure 3: Detailed drawing of a membrane module stack containing eight membrane modules.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	>11,000 (real coal)	>13,000 (real and simulated coal)
Manufacturing Cost for Membrane Material	$/m^2	50	20
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	1,700
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5

Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame (crossflow and countercurrent)	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flow rate	kg/hr	2,676	
CO_2 Recovery, Purity, and Pressure	%/%/bar	75, >85, 1 (test system conditions)	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Figure 4 shows a simple process flow diagram for the MTR engineering-scale system to be installed at TCM. A slipstream of flue gas is sent to the membrane system (stream 1). After passing through a feed blower, the flue gas (stream 2) goes to the first membrane step, where a vacuum on the permeate is used to remove CO_2. The membrane permeate (stream 4) is sent to a second-stage CO_2 purification unit (stream 5). Some of this purified CO_2 can be routed through a spillback line (stream 9) to the front of the membrane system to increase the concentration of CO_2 in the feed from 13 to ~20%. In this way, the feed to the membrane system will mimic the fully integrated case without having to recycle CO_2 to the boiler. With this spillback option, the 20% CO_2 membrane feed contains about 1 MWe worth of CO_2. The partially treated flue gas that leaves the first membrane step (stream 3) is then sent to the sweep membrane unit. Air (stream 6) flows on the permeate-side of these membranes and removes additional CO_2 from the flue gas. The CO_2-enriched air (stream 7) would be sent to the boiler in integrated operation, but here it is just vented after analysis. Finally, the cleaned flue gas (stream 5) flows to the stack.

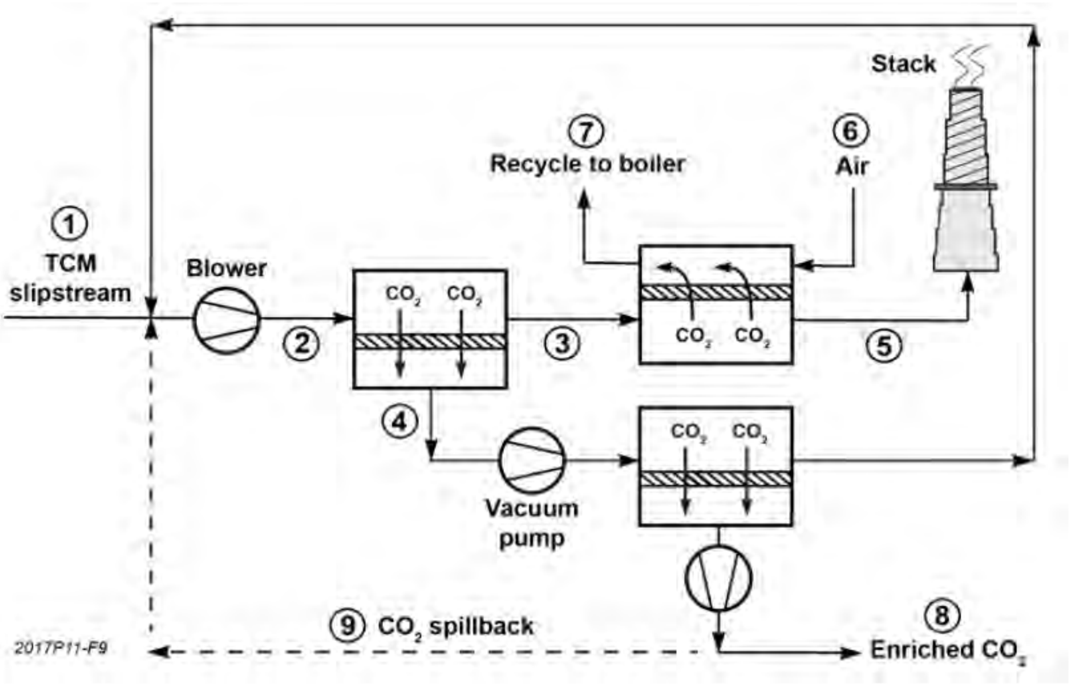

Figure 4: Simplified process flow diagram for the MTR skid operating at TCM.

Finally, the economics data for the developed membranes is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54	43
Cost of Carbon Avoided	\$/tonne CO_2	97	80

Capital Expenditures	\$/MWhr	23.9	18.4
Operating Expenditures	\$/MWhr	25.9	22.2
Cost of Electricity	\$/MWhr	50	50

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is still under investigation. Polaris modules exposed to coal-fired fuel gas at NCCC for more than a year had no reduction in performance.

Flue Gas Pretreatment Requirements – When placed downstream of existing power plant flue gas emission treatment unit operations to remove particulates (nitrogen oxide [NO_X] and SO_2). The MTR Polaris post-combustion CO_2 capture membrane process design does not require additional pretreatment.

Membrane Replacement Requirements – MTR has installed hundreds of commercial membrane systems in the petrochemical, refinery, and natural gas industries over the past 30 years. The membrane module lifetime is estimated to be three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The MTR capture process will produce a dry, CO_2-depleted flue gas stream routed to the stack and a liquid stream containing much of the moisture in the flue gas (because the MTR membrane captures water as well as CO_2). Prior studies have determined that this water can be recycled to existing flue gas desulfurization (FGD) blowdown wastewater treatment.

technology advantages

- Polaris Gen-2 membranes have a CO_2 permeance approximately 70% higher than Gen-1 and nearly 20 times that of conventional membranes.
- There are no hazardous chemicals or emissions in the membrane process.
- The plate-and-frame membrane module minimizes pressure-drop.
- A simple system allows for low-cost partial capture, while a novel two-step design efficiently captures CO_2 at high removal rates.
- The CO_2 recycle increases feed concentration, reducing membrane area and energy requirements.
- High turndown and rapid response to dynamic conditions are possible.
- The membrane module stack reduces module space and cost, which translates into additional cost savings in the system due to reduced ductwork and system complexity.

R&D challenges

- Optimizing CO_2 capture rate to minimize capture cost.
- Long-term stability of Gen-2 membranes.
- High-permeance membrane is required to lower capital cost.
- Pressure-drops must be minimized to reduce energy losses.
- Balance of plant equipment cost and efficiency, particularly for rotating equipment, are critical to system performance.
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves, and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-MWe plant.

status

The test system at TCM was fully commissioned at the end of July 2021. All budget period 2 objectives were completed, and full testing has begun. Project duration was extended to ensure at least six months of full-scale testing. The current system can capture 75% of CO_2 emissions with a CO_2 purity of more than 90%.

available reports/technical papers/presentations

Merkel, T., 2021, “Scale-Up Testing of Advanced Polaris Membrane CO_2 Capture Technology.” Quarterly Progress Report to NETL. October 29, 2021.

Casillas, C.; Hicks, D.; Huang, I.; Hofmann, T.; Kniep, J.; Merkel, T.; Paulaha, C.; Salim, W.; Westling, E., 2021, “Scale-Up and Testing of Advanced Polaris Membranes at TCM (DE-FE0031591).” Presented at the 2021 Carbon Management and Oil & Gas Research Project Review Meeting. Pittsburgh, PA. August 12, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Merkel.pdf*.

Merkel, T., et al. “Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/T-Merkel-MTR-Advanced-Polaris-Membrane-r1.pdf*

Merkel, T., et al. “Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology,” Project Kickoff Presentation, Pittsburgh, PA, September 2018. *https://www.netl.doe.gov/sites/default/files/netl-file/FE0031591-Project-Kickoff-092418.pdf*.

Merkel, T., et al. “Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology,” presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/netl-file/T-Merkel-MTR-Advanced-Polaris-Membrane.pdf*.

Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses

primary project goal

Linde Gas North America, LLC and their project partners evaluated three flue gas aerosol pretreatment technologies that have the potential to significantly reduce high flue gas aerosol concentrations, which have been shown to contribute to amine losses in solvent-based post-combustion carbon dioxide (CO_2) capture (PCC) processes. The objectives of this project were to design, build, and independently test these technologies at a coal-fired power plant host site using a slipstream of flue gas containing high concentrations of aerosol particles (greater than 10^7 particles/cm^3). The impact of this reduction in aerosol concentrations could be leveraged across a variety of solvent-based PCC systems to minimize solvent losses.

technical goals

- Perform a literature study to identify mechanisms that contribute to aerosol particle nucleation and growth in flue gas streams.
- Develop a model to simulate the mechanisms and assess the impact of aerosols on amine losses based on particle size distribution and particle number concentration.
- Complete basic engineering and design and provide cost estimates for the three aerosol pretreatment technologies selected for testing at the Abbott Power Plant.
- Fabricate, install, and commission the high-velocity water spray-based system, ESP system, and sorbent technology system at the host site.
- Perform independent parametric testing of each aerosol pretreatment technology, evaluate test results, and identify the optimum operating and design conditions for maximum performance of each technology.
- Compare test results against predefined targets and standard capabilities of conventional aerosol treatment methods described in literature and complete a techno-economic evaluation for each system to compare system costs at scale.
- Dismantle and remove pilot equipment from the host site.

technical content

Aerosol mitigation methods to reduce aerosol-driven amine losses include: (1) baghouse installation in the flue gas upstream of the PCC plant; (2) amine wash sections and wash section operating conditions for the PCC plant absorber; (3) specific absorber operating temperature and pressure conditions that can also negatively impact specific regeneration energy; and (4) flue gas aerosol pretreatment, which is the focus of the proposed technologies and testing.

Three options were evaluated in this project: (1) a novel high-velocity water spray concept previously tested at a Rheinisch-Westfälische Elektrizitätswerk (RWE) power plant in Niederaussem, Germany; (2) an innovative electrostatic precipitator (ESP) with optimized operating conditions; and (3) a non-regenerative sorbent-

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Flue Gas Aerosol Pretreatment

participant:
Linde Gas North America, LLC

project number:
FE0031592

predecessor projects:
N/A

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partners:
University of Illinois at Urbana-Champaign; Washington University in St. Louis; InnoSepra LLC; Affiliated Construction Services

start date:
06.01.2018

percent complete:
100%

based sulfur oxide (SO_X) and nitrogen oxide (NO_X) removal technology with potential for aerosol particle reduction.

Figure 1 shows the range of upstream flue gas aerosol particle number concentrations able to be managed by current methods used today to achieve less than 0.3 kg amine emitted per tonne of CO_2 captured for solvent-based PCC processes. For power plants without baghouses producing flue gas containing particle concentrations greater than 10^7 particles/cm^3, the only realistic option available to mitigate aerosol-driven amine losses from PCC plants is flue gas aerosol pretreatment. Flue gas aerosol pretreatment has traditionally been performed using simple ESPs and Brownian filters, but no systematic study has been performed to evaluate the performance of these systems over the complete range of possible operating conditions, aerosol particle number concentrations, and aerosol particle sizes. It is important to note that even with lower flue gas aerosol number concentrations (fewer than 10^7 particles/cm^3), there is still a sizeable benefit to using pretreatment systems to minimize amine losses for the entire range of solvent-based PCC operating conditions. Hence, this project focused on evaluation of flue gas aerosol pretreatment solutions to determine an optimum technology that can minimize aerosol-driven amine losses for any power plant, including plants producing flue gas with the highest range of possible flue gas aerosol concentrations and size distributions. Based on previous 1.5-megawatt-electric (MWe) pilot-scale tests of the Linde-BASF PCC technology at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, from 2015–2016, high aerosol concentrations in the size range of 70–200 nm contributed most significantly to amine losses. Hence, this technology development project targeted high removal efficiency for particles in and around this size range. Additionally, previous aerosol number concentration measurements performed at the Abbott Power Plant host site, a power generating unit without a baghouse, showed the presence of very high aerosol concentrations (greater than 10^7 particles/cm^3). The ability to apply pretreatment technologies on the wide range of aerosol concentrations measured at Abbott will enable demonstration of the performance of each technology as applied at most coal-fired power plants in the world based on aerosol measurement data collated from scientific literature.

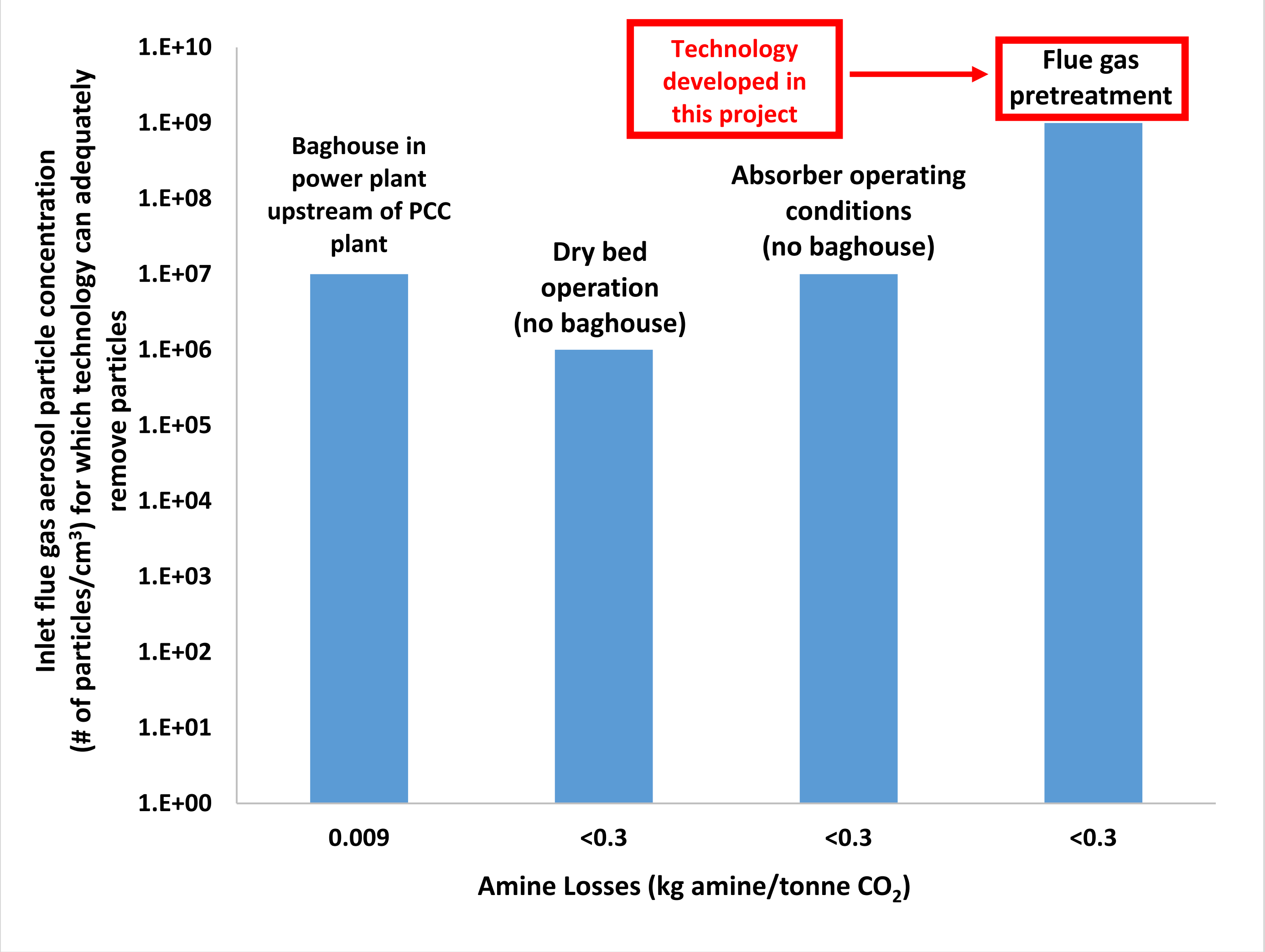

Figure 1: Flue gas aerosol particle number concentration ranges for which aerosol mitigation technologies are applicable and sufficient.

The first aerosol pretreatment technology tested in this work was a novel high-velocity water spray-based system originally developed by RWE and previously tested by RWE in Niederaussem, Germany. A process flow diagram of this system is shown in Figure 2. The high-velocity water spray provided by the specialized nozzle distributor design enables rapid growth and collection of aerosol particles in the liquid phase through water condensation before further removal by the demister at the top of the spray column. In addition, the perforated tray at the midsection of the column optimizes vapor-liquid distribution to enhance aerosol removal. Aerosol particles collected in the liquid phase are discharged in the process condensate removed from the column, effectively removing the aerosols from the treated flue gas exiting the top of the vessel. The project team has designed, constructed, and tested the water spray-based system on up to 1,000 standard cubic feet per minute (scfm) of actual flue gas emitted from two coal-fired boilers at the Abbott Power Plant host site. Parametric tests have been performed evaluating the impact of specific spray nozzle and perforated tray designs and operating conditions to determine the optimal system configuration and design conditions maximizing aerosol particle removal efficiency for very high flue gas particle concentrations (up to and greater than 10^7 particles/cm^3) for aerosol particles in the 70–200 nm diameter size range.

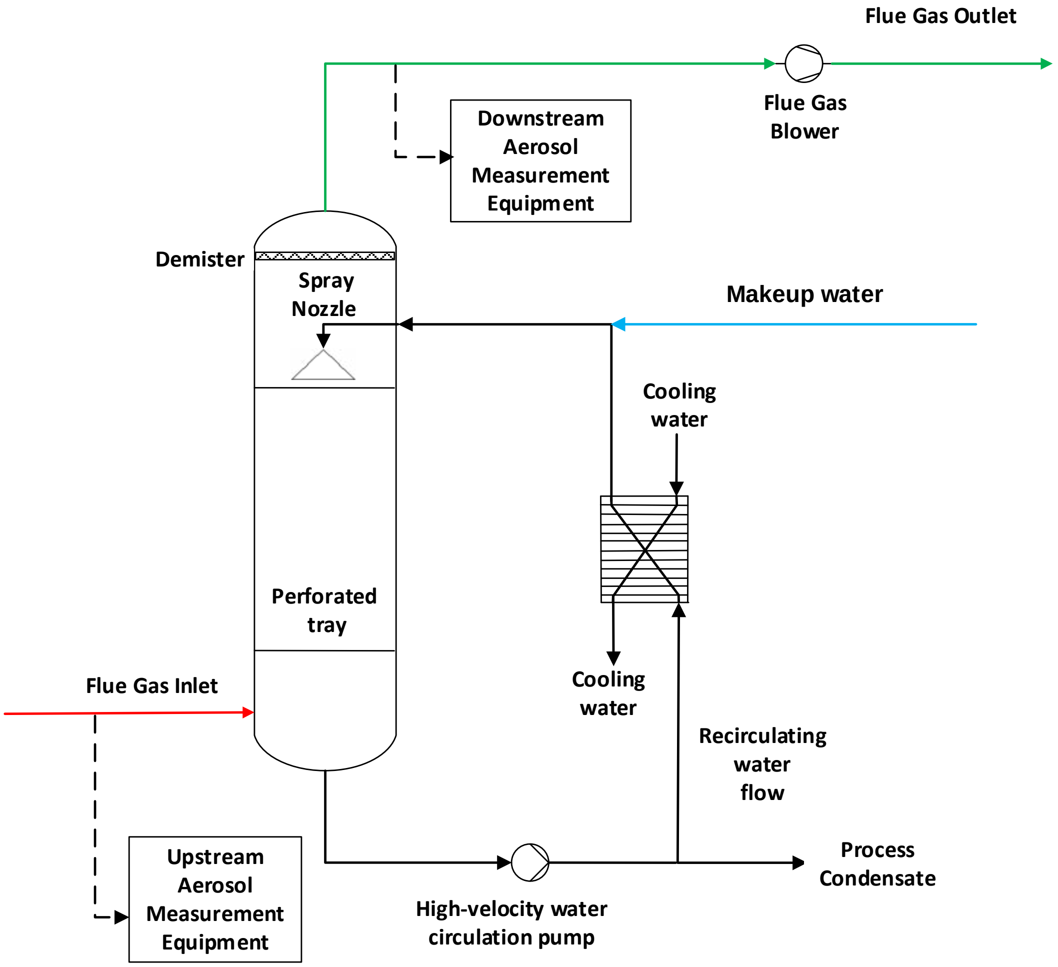

Figure 2: Process flow diagram of high-velocity water spray-based aerosol pretreatment system.

The second aerosol pretreatment technology tested in this project was an advanced ESP system developed by Washington University in St. Louis (WUSTL) that incorporated a patented photo-ionizer technology to enhance aerosol removal efficiency. The ESP functions by applying a high voltage between a plate and a wire. This voltage ionizes aerosol particles in the entering flue gas. Due to electrostatic force, ionized particles are diverted from the gas towards collecting plates, removing them from the gas. The specific collection area (SCA) of an ESP was the most important design parameter in terms of achieving required aerosol removal efficiency. A typical SCA for an ESP capable of obtaining 98–99% removal efficiency for 1,000 scfm gas flow is approximately 95 $m^2/(m^3/s)$; the area can be increased further to remove particles in the range of 10–500 nm at very high efficiencies. The pilot-scale ESP system will be tested to remove aerosol particles from flue gas at a capacity of 500 scfm. The photo-ionizer device is expected to greatly enhance the capture efficiency of nano-sized particles. In full-scale applications, the photo-ionizer developed by WUSTL can be retrofitted to existing ESPs at commercial power plants, reducing the capital costs of implementation.

A process flow diagram of the WUSTL ESP is shown in Figure 3. Specific ESP voltages may increase particle concentrations for certain particle sizes due to secondary aerosol generation inside the ESP from nucleation of water-sulfuric acid (H_2O-H_2SO_4) aerosols when sulfur dioxide (SO_2) present in the flue gas is oxidized. Hence, the ESP voltage needs to be carefully optimized during pilot tests. This project will determine the optimum design and operating conditions for the ESP system to treat flue gas with high aerosol concentrations. Through parametric testing, the performance of the advanced ESP was compared against predefined aerosol removal efficiency targets. In addition, the costs to incorporate the ESP technology upstream of a PCC plant was assessed.

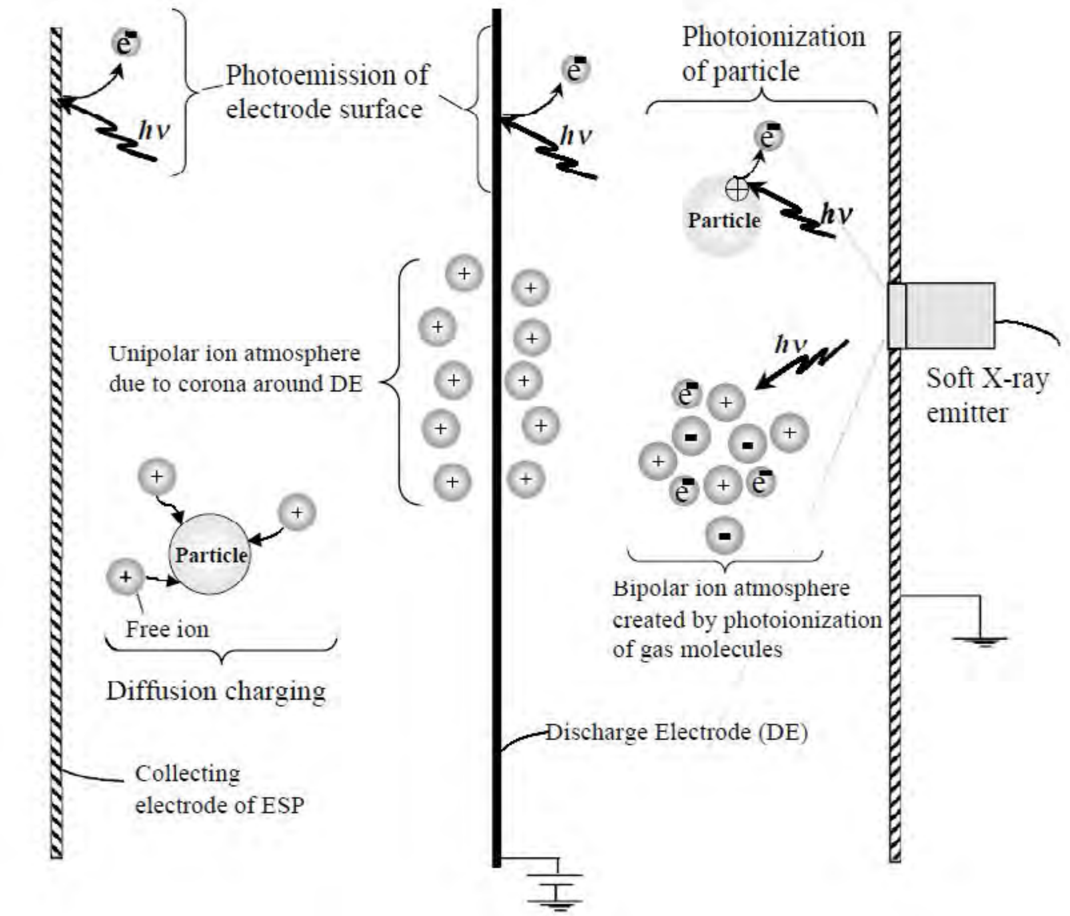

Figure 3: Conceptual flow diagram of the advanced ESP system developed by WUSTL.

The third technology tested in this project was a non-regenerative sorbent filter system developed by InnoSepra LLC. It has been proven to remove residual sulfur trioxide (SO_3), SO_2, nitrogen dioxide (NO_2), hydrogen chloride (HCl), and hydrogen fluoride (HF) from flue gas after the power plant flue gas desulfurization (FGD) unit to limit the detrimental impact of PCC solvent components reacting with flue gas contaminants. In addition to contaminant removal, the aerosol removal efficiency of the InnoSepra sorbent filter technology was evaluated as a potential means to limit aerosol-driven amine losses. A process flow diagram of the InnoSepra sorbent-based filter technology is depicted in Figure 4.

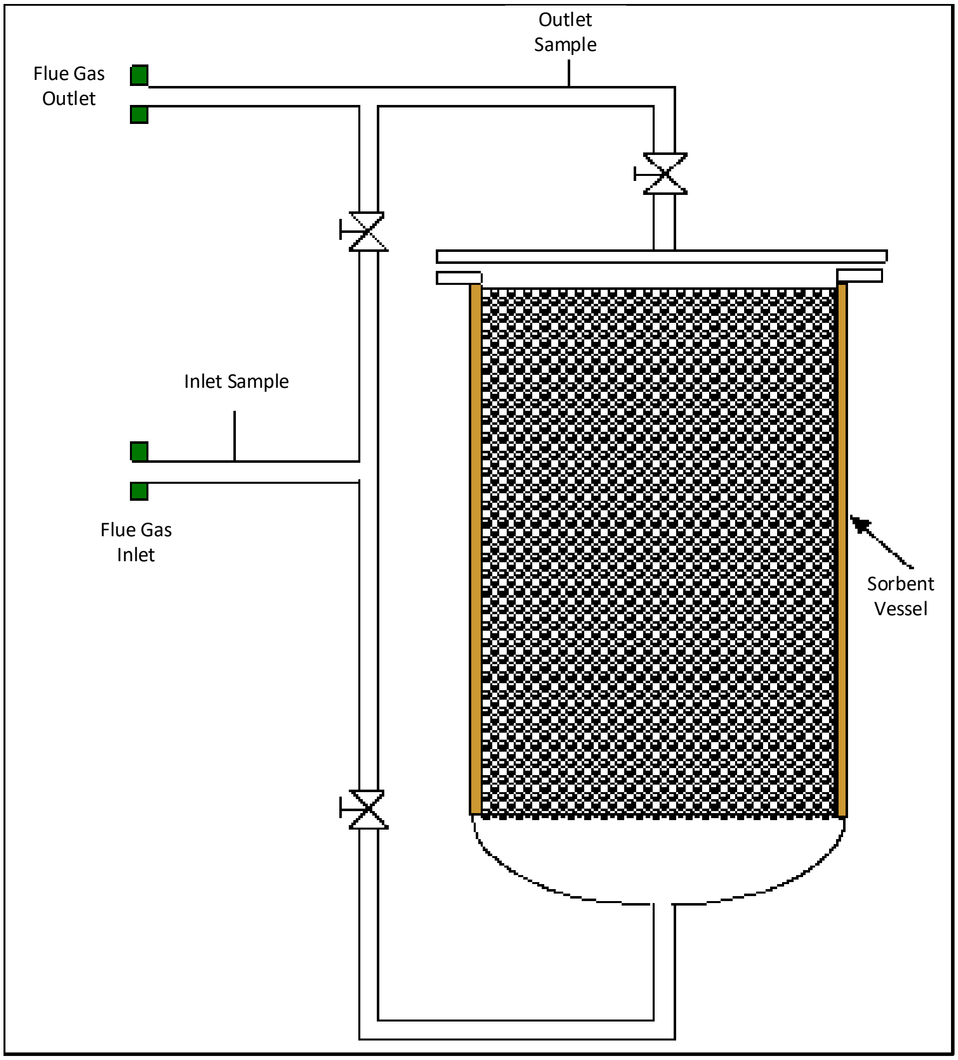

Figure 4: Process flow diagram of the InnoSepra sorbent-based filter technology.

The host site chosen for the testing was the University of Illinois' Abbott Power Plant located in Champaign, Illinois. As shown in Figure 5, Abbott's own ESPs and a wet jet bubbling FGD scrubber are used to remove some SO_2 and large particulate matter from the flue gas. The pilot testing withdraws the flue gas from the outlet of the reheat burner at the flue gas stack and returns it downstream, as Figure 5 depicts. Abbott flue gas composition, temperature, and pressure at the inlet to the aerosol pretreatment units are listed in Table 1 (based on data collected when two out of three boilers are in operation). Each technology will be built in modules and installed at the Abbott site connected to common flue gas inlet and outlet piping.

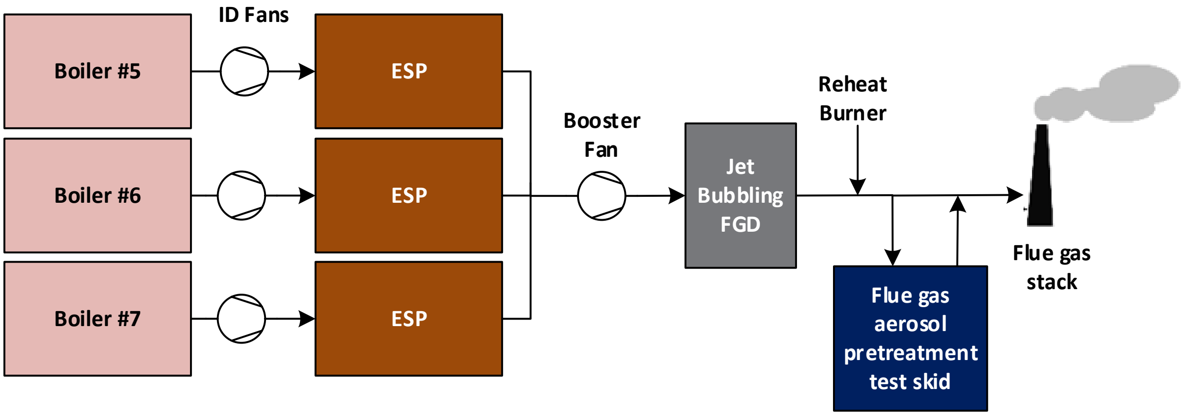

Figure 5: Abbott Power Plant layout and connection to flue gas aerosol pretreatment test skid.

TABLE 1: ABBOTT FLUE GAS PROPERTIES

Parameter	Unit	Value
Temperature	°F	200
Pressure	psig	0.75
Gas composition		
H_2O	vol%	19.2
CO_2	vol %, dry	9.2
O_2	vol%, dry	7.35
SO_2	ppmv, wet	177
NO_X	ppmv, wet	211

Preliminary performance targets for the three flue gas aerosol pretreatment systems are listed in Table 2. Cost competitiveness and environmental sustainability targets were based on scaled-up commercial versions of each technology for performance comparison with the U.S. Department of Energy's (DOE) National Energy Technology (NETL) Case B12B reference excluding baghouse capital and operating costs. From an allotted test period of eight weeks, four consecutive weeks of parametric testing were planned for the water spray-based system, two consecutive weeks of testing were planned for the ESP system, and one to two weeks of testing were planned for the InnoSepra sorbent filter system. Each technology underwent parametric testing to examine their impact on particle removal efficiency, overall capital and operating costs, and environmental sustainability performance.

TABLE 2: PRELIMINARY PERFORMANCE TARGETS FOR AEROSOL PRETREATMENT TECHNOLOGIES TESTED AT ABBOTT

Performance Parameter	Target for High-Velocity Water Spray Aerosol Pretreatment Technology	Target for ESP-Based Aerosol Pretreatment Technology	Target for InnoSepra Filter Aerosol Pretreatment Technology
Particle removal efficiency (%)[1] for 500–1,000 scfm flue gas slipstream	>98% for aerosol particles 70–200 nm in diameter		
Cost of Electricity[2]	<$133.20/MWh		
Cost of CO_2 Captured[3]	<$58/tonne CO_2		
Energy consumption	<14 MWe		
Environmental sustainability[4]	process condensate adequately removed and treated	ESP solids adequately removed	sorbent material inventory safely managed

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

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[1] (# of particles/cm^3 before aerosol treatment - # of particles/cm^3 after aerosol treatment) / (# of particles/cm^3 before aerosol treatment)

[2] when integrated with PCC technology for 550-MWe pulverized coal supercritical power plant without a baghouse

[3] when compared to DOE-NETL Case B12B without a baghouse

[4] when integrated with PCC technology for 550-MWe pulverized coal supercritical power plant without a baghouse

Pressure	Temperature	Composition						
		vol%, wet					ppmv, wet	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
15.45	200	7.4	19.2	66.6	5.9	0.80	200	211

Other Parameter Descriptions:

Flue Gas Pretreatment Requirements – The proposed work will provide as a test option effective flue gas SO_X and NO_X removal achieved using the already pilot-validated, low-cost, high-capacity, non-regenerative InnoSepra sorbent material installed in a packed bed upstream of the test skid. In addition to the physical effects of the sorbent bed on aerosol removal, the InnoSepra sorbent can improve aerosol reduction performance by reducing nucleation of H_2SO_4 aerosols in the flue gas by minimizing its SO_X content.

Waste Streams Generated – Acidic process condensate is generated by the high-velocity water spray-based system in a similar manner to how a direct contact cooler operates upstream of a solvent-based PCC plant. This condensate contained nitric acid (HNO_3) and H_2SO_4 from reaction of NO_X and SO_X in the flue gas with the circulated process water used in the spray column. This water was sent to Abbott's onsite water pretreatment facility where it was neutralized. The ESP plates collected a very small mass of solid particles during operation on coal-fired flue gas. The solids collected include metal oxides, dust, and other contaminants. These were easily removed from the plates and discarded in the power plant's gypsum pile. The InnoSepra sorbent material must be removed after use and sent to the vendor's processing facility to either be specially processed for reuse or discarded in an approved manner compliant with all waste management regulations.

Process Design Concept – See above.

technology advantages

- Mitigates a wide range of flue gas aerosol concentrations and size distributions, including very high concentrations (up to and above 10^7 particles/cm^3) in the 70–200 nm particle size range.
- Reduced solvent makeup requirements lower operating expenditures for solvent-based PCC processes, enhance PCC performance in terms of energy consumption, reduce the need for solvent reclamation units, and improve solvent inventory logistics for full-scale operations.
- Reduced solvent emissions to the environment and aerosol contaminant exposure to personnel and environment.
- Smaller process footprint, more cost-effective, flexible operation, and higher aerosol removal efficiency compared to installing a baghouse at a coal-fired power plant.

R&D challenges

- Waste management.
- Effects of variability in flue gas composition, temperature, and pressure, as well as power plant load changes on aerosol measurements.
- Material compatibility with corrosive flue gas contaminants.

status

A comprehensive summary of the results from the aerosol-driven amine loss mechanisms study and modeling effort, as well as the environmental health and safety (EHS) analysis, were completed. Basic and detailed engineering for the Linde spray-based system, ESP-based system, and InnoSepra filter system were completed by Affiliated Construction Services (ACS), WUSTL, and InnoSepra, respectively. All pilot equipment procurement and fabrication activities were completed, and all pilot system components were delivered to the Abbott site and installed on a concrete pad. Pilot system commissioning and test-readiness checks were completed.

Pilot tests have shown that the RWE high-velocity water spray tower technology can achieve 85–90% aerosol removal efficiency within the 70–200 nm size range of interest for mitigating aerosol-driven amine losses from solvent-based PCC plant. The WUSTL ESP technology demonstrated removal efficiencies up to 80% at the highest voltage tested, but the

ESP field tests were limited by the actual voltage that could be applied due to electrical arcing as a result of insufficient insulation. The InnoSepra sorbent filter was able to achieve greater than 99% SO_2 removal from the flue gas and aerosol removal efficiencies of 30–90% within the 70–200 nm size range.

available reports/technical papers/presentations

Bostick, D. "Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses," Project Kickoff Meeting, Pittsburgh, PA, July 2018. *http://www.netl.doe.gov/projects/plp-download.aspx?id=10433&filename=Flue+Gas+Aerosol+Pretreatment+Technologies+to+Minimize+(PCC)+Solvent+Losses.pdf*.

Bostick, D. "Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses," NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/D-Bostick-Linde-Flue-Gas-Aerosol-Pre-Treatment.pdf*.

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Engineering-Scale Demonstration of the Mixed-Salt Process for CO_2 Capture

primary project goal

SRI International is developing a novel ammonia (NH_3) and potassium carbonate (K_2CO_3)-based mixed-salt solvent carbon dioxide (CO_2) capture process. Large bench-scale and small pilot-scale (~0.5 megawatt-electric [MWe]) testing is being performed to validate enhanced CO_2 capture efficiency, high loading capacity, and reduced energy consumption.

technical goals

- Demonstrate the individual absorber and regenerator processes for NH_3 and K_2CO_3 solvent systems with high efficiency, low NH_3 emissions, and reduced water use compared to the state-of-the-art, NH_3-based technologies.
- Establish a rate-based thermodynamic modeling database for the potassium- and NH_3-based system heat and mass balance evaluations.
- Demonstrate the completely integrated absorber-regenerator CO_2 capture system at the bench-scale and optimize the system operation.
- Test two alternative flowsheets for process optimization, test system at highest possible CO_2 loadings, and determine steam usage for regeneration.
- Test the continuous operation of the process in an integrated absorber-regenerator system.
- Field-test the mixed-salt process (MSP) at engineering scale to determine process operability under both dynamic and steady-state conditions using actual flue gas.
- Test the process with advanced heat integration for improved process efficiency and determine optimal regeneration energy requirement.
- Optimize the engineering-scale operation of the MSP to achieve high capture rate, high cyclic CO_2 loading, and high-purity CO_2 stream at high pressure.
- Evaluate solvent and water management strategies.
- Collect data to perform the detailed techno-economic analysis (TEA) of CO_2 capture process integration to a full-scale power plant.

technical content

SRI International is developing a novel mixed-salt solvent-based technology for post-combustion CO_2 capture using a non-degradable solvent that combines readily available, inexpensive potassium and NH_3 salt solutions and employs a novel flow configuration that is optimized to improve absorption kinetics, minimize NH_3 emissions, and reduce water use compared to state-of-the-art, NH_3-based and amine technologies. The solvent and process parameters are provided in Table 1.

A singular NH_3-based process, such as chilled NH_3, has several advantages (e.g., very high CO_2 loading capacity, reduced reboiler duty due to high-pressure regeneration, and fast absorption kinetics). Challenges of this process include the need for a large water wash to reduce NH_3 emissions, requirement to chill the

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Ammonia and Potassium Carbonate-Based Mixed Salt Solvent

participant:

SRI International

project number:

FE0031588

predecessor project:

FE0012959

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partners:

Technology Center Mongstad (TCM); Baker Hughes (BH); Politechnico di Milano (PoliMi); OLI Systems Inc.; Aqueous Solutions Aps (ASAps)

start date:

07.01.2018

percent complete:

60%

solvent, and energy usage for solid dissolution. A singular K_2CO_3-based process offers several advantages (e.g., no emissions, long-term industrial use, and simple permitting). However, this process has lower efficiency and CO_2 loading, as well as energy requirements for solid dissolution and vacuum water stripping. By combining these two solvent technologies, SRI capitalizes on the advantages of each while minimizing the drawbacks. The MSP maintains the high CO_2 loading and enhanced absorption kinetics, delivering high-pressure CO_2 in a solids-free system. The rate of CO_2 absorption is enhanced by having NH_3 act as a promoter that shuttles the CO_2 to the carbonate ion in the solution across the gas/liquid interface and increases the partial pressure of CO_2 in the dissolved phase. This increases the rate of CO_2 collision with carbonate ion and results in an increase in the rate of CO_2 absorption. Furthermore, by combining the salts, the capture system experiences reduced reboiler and auxiliary electricity loads, reduced NH_3 emission, reduced water usage, and a reduced system footprint.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.17	0.17
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.27-0.35	0.35
Specific Gravity (15°C/15°C)	—	1.1-1.3	1.1-1.3
Specific Heat Capacity @ STP	kJ/kg-K	3.0-4.0	3.0-4.0
Viscosity @ 15°C	cP	1.6	1.6
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	25-40
Equilibrium CO_2 Loading	mol/mol	0.6 (rich)	0.6 (rich)
Heat of Absorption	kJ/mol CO_2	1,000–1,200	<1,200
Solution Viscosity	cP	1.5-1.8	<1.9
Desorption			
Pressure	bar	10-15	10
Temperature	°C	120-170	120-170
Equilibrium CO_2 Loading	mol/mol	0.2 (lean)	<0.2 (lean)
Heat of Desorption	kJ/mol CO_2	1,000-1,200	<1,200
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 ~20	
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Taking into consideration the key advantages discussed above, the regenerator energy requirement was estimated and compared to monoethanolamine (MEA)-based and pure K_2CO_3-based processes. Figure 1 shows a significant reduction in regenerator heat requirement for the MSP. In the MSP, the sensible heat is lower than that of MEA-based technology because the MSP is operated with very high CO_2 loading and lean regeneration; thus, a lower volume of solvent is required to carry the CO_2. In addition, since the regenerator operates at a higher pressure in the MSP, the reflux ratio is very low (water $[H_2O]/CO_2$ less than 0.01); therefore, the heat of evaporation is insignificant. The heat of reaction is considerably lower for MSP compared to amine processes, leading to further reduction in reboiler heat duty. Another key difference in the MSP is that, unlike chilled NH_3 or a neat K_2CO_3-based process, the MSP is designed to operate without solids in the absorber, eliminating additional heat requirement for solid dissolution in the regenerator or heat exchangers.

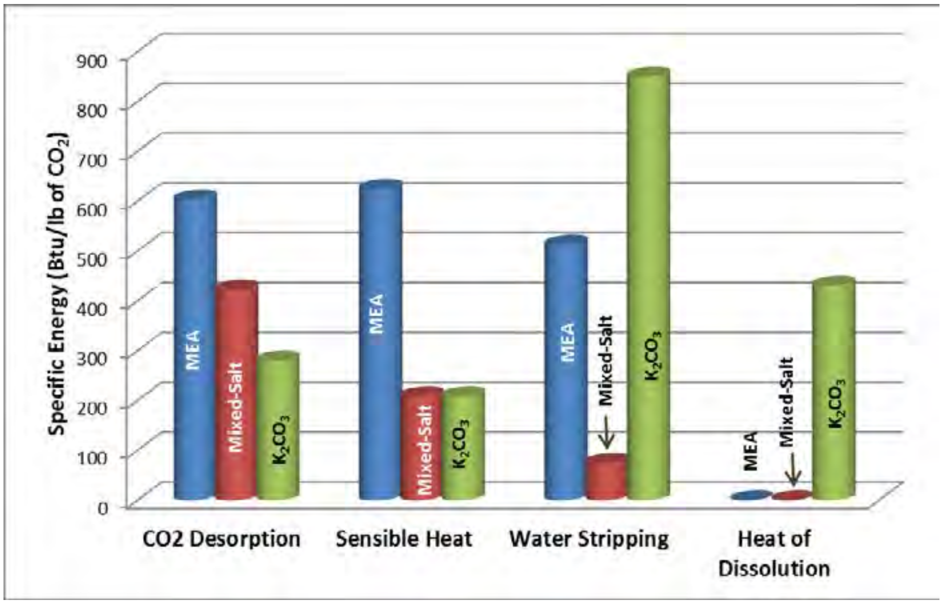


Figure 1: Estimated regenerator heat requirement for mixed-salt system with 0.2–0.6 cyclic loading of CO_2.

The MSP system, shown in Figure 2, comprises two isothermal absorbers, a selective regenerator, and auxiliary equipment. The absorbers operate with different ammonia to potassium ratio (NH_3/K) solutions formulated to maximize the absorption and minimize the NH_3 loss. The absorber system is designed to integrate downstream of a flue-gas desulfurization (FGD) unit in a pulverized coal power plant. The CO_2 in the flue gas stream is absorbed in the absorber columns, which are operated with liquid recycle and heat exchangers to remove the heat of reaction and keep the solution at the optimum temperature for efficient absorption and minimum NH_3 slip. The CO_2-rich solutions from the absorbers are sent to the regenerator for CO_2 stripping and solvent regeneration. The MSP uses a selective regenerator to regenerate two CO_2-lean salt streams with different NH_3/K ratios. These streams are drawn from a lower-middle stage and the bottom stage of the regenerator. The regenerator is operated at high-pressure, isobaric conditions, and has a temperature gradient along the height of the column. The key advantage of the MSP regenerator design is to capture the latent heat within the regenerator before the stream exits the vessel, thus generating almost dry CO_2 stream (H_2Ovap/CO_2 less than 0.2) at high pressure, reducing both operational and capital CO_2 compression costs. The overall benefit of MSP is a significant reduction in the cost of the CO_2 capture.

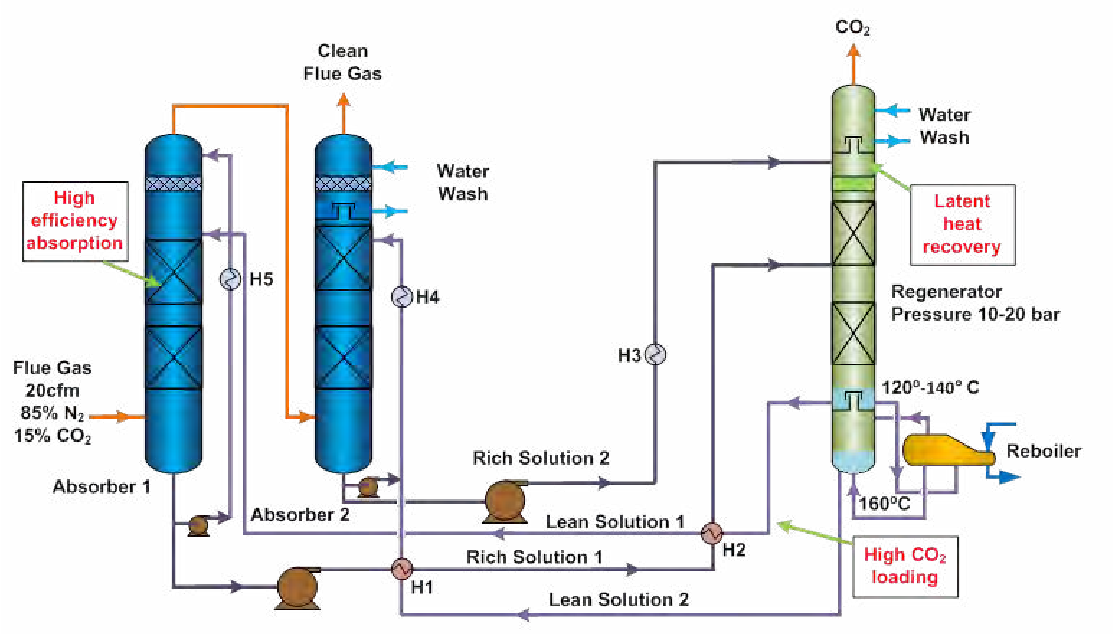


Figure 2: SRI mixed-salt simplified process diagram.

Bench-scale operation of the individual absorber and regenerator units provided optimized process parameters prior to the design and testing of the large bench-scale integrated absorber-regenerator system. The absorber was operated near ambient temperature and the regenerator was operated up to 160°C. The absorber system (Figure 3) has two absorber columns (8-inch diameter) that are designed to operate independently with different absorption solutions, and the gas stream passes through them in series. The dual absorber system operates with a high NH_3/K ratio solution in the first absorber and low NH_3/K ratio solution in the second absorber, which results in a reduction in NH_3 loss from the absorbent solution compared with a single solution approach, as shown in Figure 4. The data from the mixed-salt absorber system testing also demonstrated that it was possible to reach greater than 90% CO_2 capture even using a solution that has fairly high CO_2 loadings (e.g., in the 0.4–0.6 range).

Figure 3: Close-up view of two absorber columns.

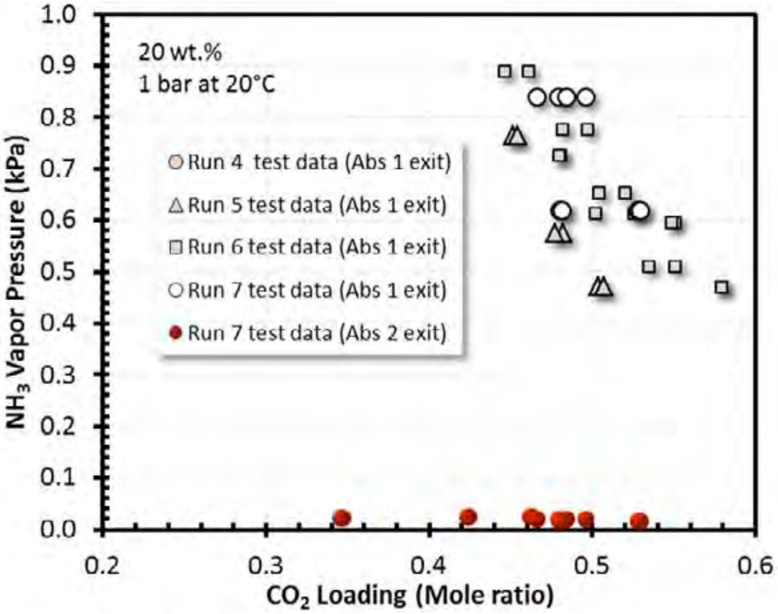
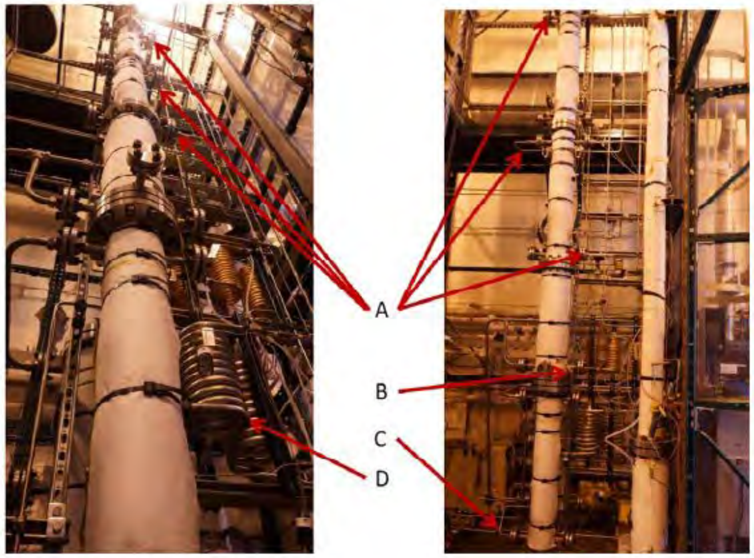


Figure 4: Measured NH_3 vapor pressure at various CO_2 loadings for tests conducted with a single absorber (Runs 4, 5, and 6) and for the test conducted with the dual absorber (Run 7).

Regenerator tests were performed with 20 and 30 wt.% mixed-salt compositions in a semi-continuous mode. Figure 5 is a photograph of the large bench-scale regenerator showing solution inlets, outlets, and heat exchangers. Figure 6 shows the number of moles of CO_2 stripped in a series of runs in the pressure ranges of 6–7 and 11–12 bar in the temperature range of 120–160°C for 20 wt% mixed-salt solutions with 0.49 CO_2 loading.



A : Rich solution inlet locations.
B : Discharge location for high NH3/K ratio solution
C : Discharge location for low NH3/K ratio solution
D: Heat exchangers (Cold rich ↔ Hot lean)

Figure 5: Large bench-scale regenerator.

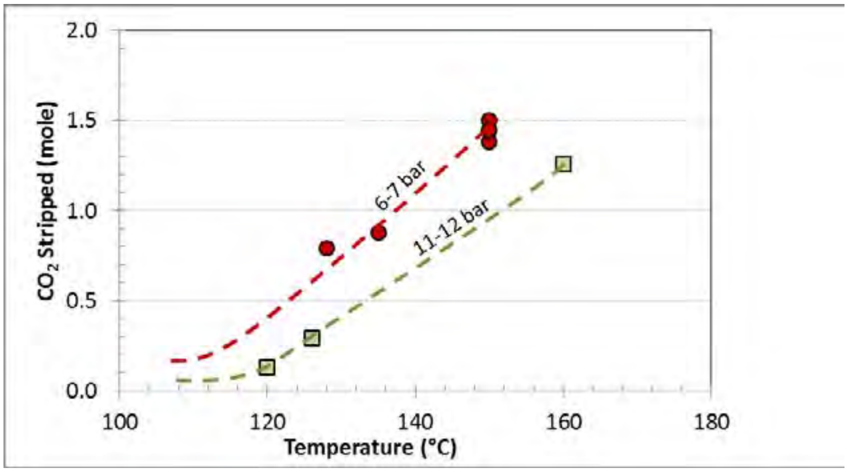


Figure 6: CO_2 stripping as a function of regeneration temperature and pressure.

The integrated bench-scale CO_2 capture and regeneration system, as depicted in Figure 2, was operated for 60 hours. The rich liquid flow from absorber 1 was split and pumped into the column at two stages with approximately 20% going to an upper stage. The rich solution from absorber 2 was cooled to approximately 15°C and pumped to the top stage of the regenerator column to reduce the NH_3 emission from the regenerator. As a polishing step, the high-pressure water wash was mounted at the very top of the regenerator such that the emitted CO_2 gas has less than 10 parts per million (ppm) NH_3 content. The lean stream with high NH_3/K ratio for absorber 1 was drawn from a lower-middle stage of the regenerator column, which was at approximately 130°C. The lean solution with low NH_3/K ratio for absorber 2 was drawn from the bottom stage of the regenerator column, and the temperature of this stage was about 160°C. The regenerator was operated under isobaric conditions with a temperature gradient, approximately 30–50°C at the top and 155–160°C at the bottom. Two main heat exchangers recovered the sensible heat from the regenerated solution to heat the incoming rich solution. The outgoing lean streams from heat exchangers were approximately 40°C, and thus they needed to be cooled to about 15–20°C before they were fed to the absorber columns. For the continuous operation of the regenerator, the input rich-solution flows and exit lean-solution flows were balanced, and the liquid levels of draw stages were carefully controlled to avoid flooding or dry-up of regenerator stages. The integrated system performed as designed with excellent absorption and regeneration cycles and demonstrated more than 90% CO_2 capture. Two variants of the MSP were tested to further decrease the NH_3 loss and water usage. In variant 1, the length of absorber 2 was increased and solvent flow recirculation was slightly modified. A water wash was also installed, with larger surface area and recirculation than the original MSP design. These changes reduced the NH_3 in the absorber exit from approximately 3,000 ppm to approximately 1,000 ppm and the NH_3 in the water wash exit to less than 10 ppm. In addition, the raw water consumption was reduced by a factor of six. In the variant 2 configuration, the CO_2-rich solution was introduced at the exit of the second absorber to reduce the NH_3 content in the gas stream leaving the absorbers. In this case, the system took longer to reach steady-state and needed higher flow rate of water in the water wash to control the NH_3 emission; thus, variant 2 was not pursued for more detailed testing.

Using the bench-scale experimental data, a rate-based model for detailed mass-balance and heat-balance calculations for a flue gas feed equivalent to a 550-MWe flue gas stream was developed and validated in OLI System's Environmental Simulation Program. Initially, OLI conducted the mass and heat balance determination for various regenerator options. The reboiler duty requirement for the best layout with 0.2–0.5 cyclic CO_2 loading operation was 2.0 (± 0.2) MJ/kg-CO_2. The technology was modeled for the CO_2 recovery facility, in which 90% of the CO_2 from the flue gas was captured from a supercritical pulverized coal plant with a nominal net output of 550 MWe (U.S. Department of Energy [DOE] Case 11). The other fixed parameters were regeneration of high-pressure CO_2 at 99% purity and an NH_3 release from the absorber that was less than 10 ppm. The study showed the technology offers much lower energy penalty than Fluor Econamine FG Plus^{SM} technology, which uses a formulation of MEA and a proprietary corrosion inhibitor to recover CO_2 from the flue gas.

A field test of the MSP at engineering-scale is being conducted using the existing Chilled Ammonia Process (CAP) infrastructure at Technology Center Mongstad (TCM) in Norway. Re-commissioning of the CAP system is required prior to conducting the field test, followed by a hazard and operability (HAZOP) evaluation. Modeling of the modified flowsheet is being performed to identify the optimal configuration for MSP implementation at TCM. The process involves modeling of individual systems blocks (absorber, regenerator, and NH_3 recovery block) separately and then integrating them with the inclusion of flow stream. The absorber block includes three absorbers. In these studies, the NH_3 emission from the water wash tower (less than 10 ppm) and the CO_2 capture efficiency (greater than 90%) were set as fixed parameters. Figure 7 shows the comparison between the CO_2 capture efficiency profiles in each of the absorbers for configurations A and B as predicted by the model.

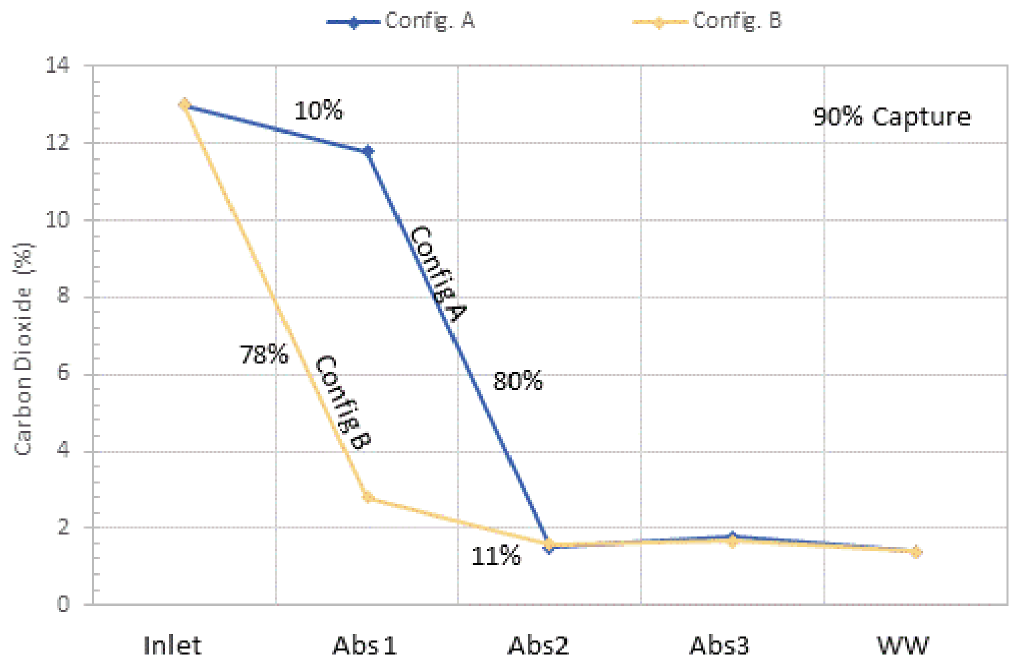


Figure 7: CO_2 capture efficiency profiles for configurations A and B (total of 90% capture in both cases).

Testing of the integrated system, along with process modeling, provided parametric optimization to update the TEA and determine costs associated with the use of this system in a 550-MWe power plant. The cost of electricity (COE) found in the analysis of the mixed-salt technology was 126.1 \$/MWh, yielding a reduction of 11.7% compared to the National Energy Technology Laboratory (NETL) Case 12B COE of 142.8 \$/MWh.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – In the MSP, CO_2 is captured by a chemical absorption that involves a series of ionic chemical reactions among CO_2, NH_3, K_2CO_3, and H_2O. The mechanism of CO_2 capture by chemical absorption using various chemical formulations has been studied extensively. The MSP chemistry comprises gas/liquid-phase mass transfer, followed by a series of chemical reactions in the liquid phase. The overall process chemistry can be summarized as:

$$K_2CO_3 - NH_3\text{-}xCO_2\text{-}H_2O + (y\text{-}x)CO_2 \leftrightarrow K_2CO_3 - NH_3\text{-}yCO_2\text{-}H_2O$$

where $y > x$

Solvent Contaminant Resistance – The solvent is expected to be resistant to several contaminants, such as sulfur oxides (SO_X) and nitrogen oxides (NO_X), nominally present in a flue gas stream. Sulfur dioxide (SO_2) reacts with the solvent, but it can be removed in the direct contact cooler section as sulfates. The resistance of the solvent to trace metals is not yet known.

Solvent Foaming Tendency – Solvent foaming tendency was not observed in the bench-scale tests.

Flue Gas Pretreatment Requirements – Unlike in an MEA system, a mixed-salt system does not require deep FGD; 200-ppm level SO_2 is acceptable.

Solvent Makeup Requirements – Mixed-salt is a mixture of NH_3 and K_2CO_3 and it is inexpensive and readily available. The loss of the solvent is expected to be less than 0.2 kg/tonne of CO_2 captured.

Waste Streams Generated – Water wash with trace ammonium sulfate from the SO_2 captured by the direct contact cooler.

Process Design Concept – See Figure 2.

technology advantages

- Low heat of reaction (35–50 kJ/mol) and low reboiler duty (~2 MJ/kg of CO_2).
- High temperature (20–40°C) absorber operation without solvent chilling.
- High CO_2 loading capacity (10 wt%).
- High-pressure regeneration of greater than 99% pure dry CO_2, resulting in reduced compression costs.
- Low sensitivity to impurities.
- Non-degradable solvent uses inexpensive, industrially available materials.
- Low NH_3 emissions using two-stage absorber approach.
- Low water usage.
- Requires no feed stream polishing.
- No hazardous waste generation.
- Uses known process engineering.
- Operates with no solids in the absorber.
- Reduced energy consumption (higher efficiency) compared to MEA.
- Reduced auxiliary electricity loads.

R&D challenges

- Residual NH_3 in the exit gas stream.
- Reduction of NH_3 evaporation at higher reaction rates.
- High-pressure drop in absorber column.

status

Budget Period 3 objectives are approaching completion. The host site has been selected and the integrated system design is being finalized, including risk assessment, process diagrams, and heat and mass balance estimates. The engineering-scale CO_2 capture plant will be installed at the Abbott Power Plant in Champaign, Illinois.

available reports/technical papers/presentations

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Safeguarding Amines from Oxidation by Enabling Technologies

primary project goal

The University of Texas at Austin is developing technologies to safeguard amine-based carbon dioxide (CO_2) capture processes from solvent loss by oxidation. The project team is evaluating strategies to minimize amine oxidation in advanced second- and third-generation solvents caused by two of the most significant impurities: oxygen and nitrogen dioxide (NO_2). These effective technologies will reduce the cost and environmental risk of solvent-based carbon capture systems by addressing the effects of flue gas impurities on solvent loss and will make significant progress toward achieving $30/tonne of CO_2 captured by 2030.

technical goals

- Develop technology to overcome amine oxidation processes which includes nitrogen sparging, optimizing time and temperature with dissolved oxygen, optimizing time and temperature at the bottom of the stripper, and in the presence of adsorbed soluble iron.
- The technology will support capture using second- and third-generation solvents from fossil fuel-fired power plants.
- Baseline experiments will consist of gas-fired turbine conditions using 5 molar (m) piperazine and the advanced flash stripper (PZAS). Further experiments will extend this work to hydroxyl-ethyl-piperazine (HEP), the blend of amino-methyl-propanol (AMP)/PZ, and other amines.

technical content

The University of Texas at Austin has been developing a CO_2 capture process (PZAS) using 5 m (30 wt%) PZ with the advanced flash stripper (AFS) (Figure 1). This solvent and process (PZAS) serves as the baseline for this project on solvent loss. Five molar PZ absorbs CO_2 two times faster and has 1.36 times greater capacity than 30 wt% monoethanolamine (MEA). The AFS requires 15–20% less heat than a simple stripper. The PZAS system has been demonstrated at National Carbon Capture Center (NCCC) coal conditions (0.5 megawatt [MW]) and natural gas combined cycle (NGCC) conditions (0.3 MW) to require a heat duty less than 2.1 gigajoules (GJ)/tonne CO_2 removed.

The PZAS process is representative of second-generation amine scrubbing technology for CO_2 capture. It is fully published and represents a valuable case study with results that will be useful for proprietary second-generation processes, such as those offered by MHI and Shell/Cansolv. This technology sheet describes general approaches to minimizing oxidation and addresses the specific objectives of this project.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Reduce Solvent Loss in Amine-Based CO_2 Capture Processes

participant:
University of Texas at Austin

project number:
FE0031861

predecessor projects:
N/A

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partners:
N/A

start date:
03.01.2020

percent complete:
58%

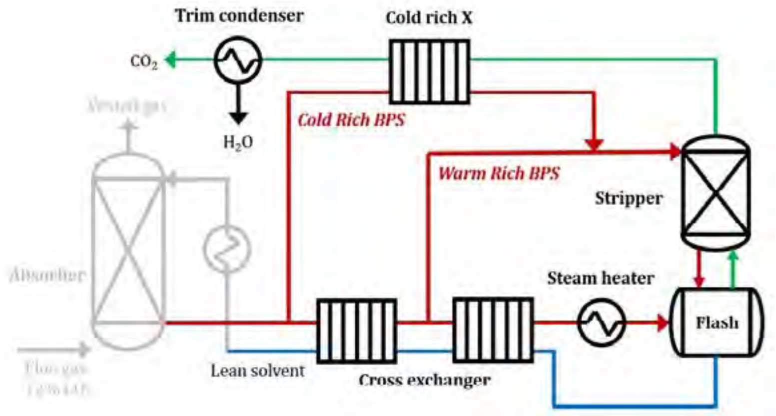

Figure 1: PZAS process.

Early bench-scale work showed that MEA, ethylenediamine, and other amines readily oxidize at 40–60°C when there is sufficient mass transfer to dissolve 0.05–0.21 bar oxygen (O_2) and some dissolved iron to initiate the free radical reaction. A necessary prerequisite for low oxidation is to select amines resistant to oxidation at 40–60°C. MHI, Shell/Cansolv, and other developers of second-generation amines have claimed that their solvents are resistant to oxidation. This project will evaluate PZ, HEP, and AMP/PZ, which have previously been shown to be resistant to oxidation.

Figure 2 shows the oxidation rate of PZ in four pilot plants as the accumulation of nitrogen degradation products. An important objective of this proposed work is to understand why there is less oxidation at the University of Texas Separations Research Program (UT-SRP) and NCCC-AFS so that those conditions can be applied to reduce oxidation at other sites, with other solvents, and with other process configurations. Four features may be responsible for low oxidation and represent opportunities that can be used commercially:

- There was no NO_2 in the flue gas at SRP and NCCC-AFS, so eliminating NO_2 may be an effective method of minimizing oxidation.
- The AFS provides flashing of the hottest solvent that removes dissolved oxygen before it reaches the maximum time and temperature in the stripper sump.
- The average residence time of hot lean solvent in the stripper sump is less than two minutes at UT-SRP and NCCC-AFS, which may minimize oxidation of amine by Fe^{+3}.
- Dissolved iron was less than 0.02 micromoles (mM) at UT-SRP and less than 0.10 parts per million (ppm) at NCCC-AFS.

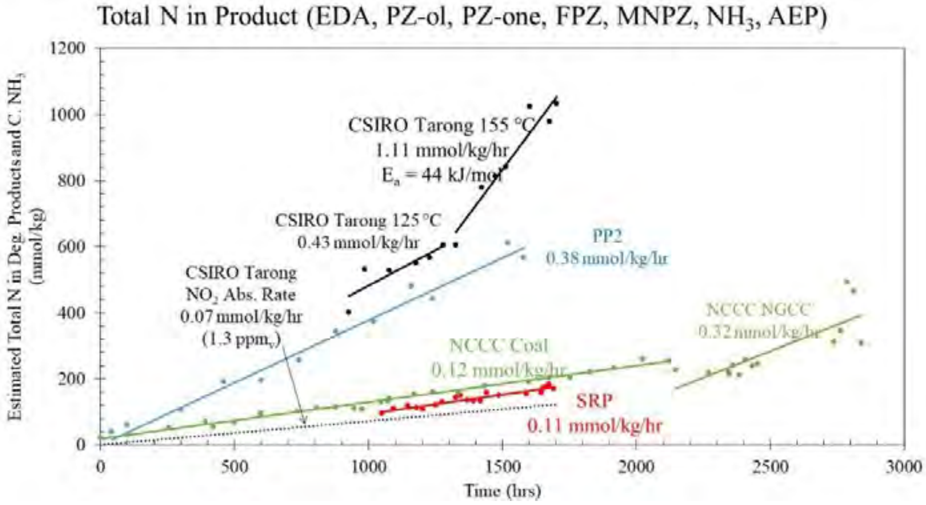

Figure 2: Total nitrogen quantified in degradation products and estimated cumulative ammonia at SRP, PP2, Tarong, and NCCC.

If an amine is resistant to oxidation at absorber conditions, rich solvent leaving the absorber sump will be saturated with oxygen at the absorber temperature (T) and P_{O2}. When heated to stripper T in the cross exchanger, the faster kinetics at elevated T will result in oxidation in the rich line before the dissolved oxygen is removed by stripping or flashing. Researchers have demonstrated that PZ and methyldiethanolamine (MDEA)/PZ will oxidize by this mechanism.

The University of Texas at Austin has demonstrated, using bench-scale testing, that nitrogen sparging in the rich solvent can reduce oxidation by a factor of 3.5–4.5 when the rich solvent is exposed to 150°C for 30 seconds without prior stripping (Figure 3). These results also establish that oxidation requires residence time at elevated temperatures and would be negligible at absorber T. It appears that oxidation could be reduced by operating the stripper at lower temperatures.

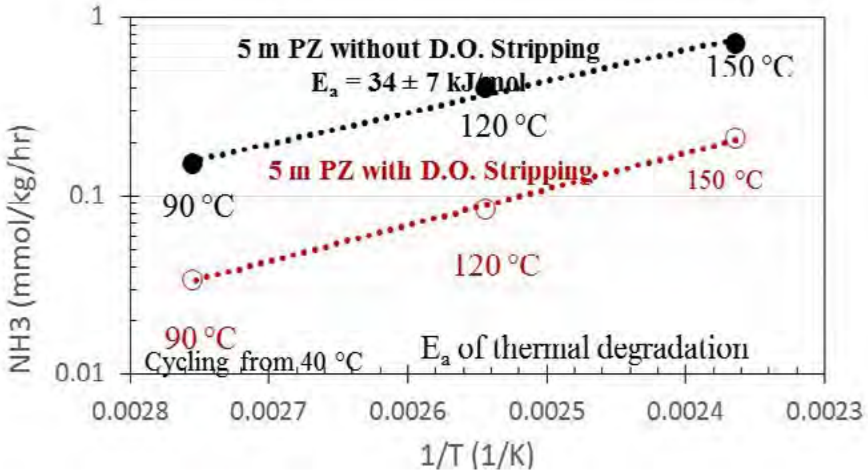

Figure 3: N_2 sparging reduces oxidation in high-temperature oxidation reactor (HTOR) by a factor 3.5–4.5. Cycling from 40°C with 0.1 mmol Fe^{+2}/kg. At 40°C absorption/40°C stripping, the ammonia (NH_3) production rate (0.025 mmol/kg-hr) would be negligible. (Nielsen, 2018)

In a pilot plant or larger-scale system, it is probable that oxidation by dissolved oxygen will occur in the hot liquid holdup between the cross exchanger and the top of the stripper where the oxygen will be removed. With a typical commercial simple stripper, the holdup in the rich feed line could be 40 sec (200 ft of pipe at 5 ft/s). However, in advanced configurations such as the AFS, the rich solvent feed can be 10–25°C colder than the stripper sump, thus reducing the oxidation rate by this mechanism, as seen at UT-SRP (Figure 2).

technology advantages

- Create environmentally friendly solvent processes for CO_2 capture.
- Safeguard second- and third-generation solvents from O_2 and NO_2 oxidation, reducing solvent degradation and extending solvent lifetime.

R&D challenges

- Using research and development (R&D) corrosion loop test results to design SRP pilot modifications for residence time tests.

status

The University of Texas at Austin developed an ultraviolet visible (UV-Vis) measurement technique as a method for evaluating metal ion (iron) species in amine solvents. Their experimental data allowed them to estimate adsorption rates and isotherms for PZ oxidation products on carbon in degraded samples. During this work, researchers also designed and developed new corrosion loop test skid and designed SRP pilot modifications for residence time tests. The project conclusions on Fe^{+2}/Fe^{+3} was the Fe^{+3} solubility in PZ varies solvent degradation from 0.02–2 mM. Carbon bed treatment reduced ammonia (NH_3) production at the NCCC and in HTOR. Carbon bed treatment removed 3 mM of "soluble" iron from the NCCC solvent system. All the "soluble" Fe must be removed to reduce oxidation. Carbon bed treatment also removed PZ degradation products that adsorb at 320 and 540 nm. In addition, greater than 0.01 m PZ protects carbon steel from corrosion at the absorber temperature.

available reports/technical papers/presentations

Rochelle, G., “Safeguarding Amines from Oxidation by Enabling Technologies,” Presented at 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Rochelle_amine.pdf*

Rochelle, G., Closmann, F., “Safeguarding Amines from Oxidation by Enabling Technologies,” Budget Period 1 Review Meeting presentation, Pittsburgh, PA, May 10, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=10928&filename=Safeguarding+Amines+from+Oxidation+by+Enabling+Technologies.pdf*.

Closmann, F., “Safeguarding Amines from Oxidation by Enabling Technologies,” Project kickoff meeting presentation, Pittsburgh, PA, June 10, 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10927&filename=Safeguarding+Amines+from+Oxidation+by+Enabling+Technologies.pptx*.

Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Solvent for Coal and Natural Gas Applications

participant:
Electric Power Research Institute

project number:
FE0031945

predecessor project:
FWP-70924

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partners:
Pacific Northwest National Laboratory; RTI International; Paul M. Mathias Consulting LLC; Gradient; Worley; Southern Company Services

start date:
10.01.2020

percent complete:
30%

primary project goal

The project goal is to demonstrate the capability of a novel water-lean solvent, comprised of more than 90 wt.% N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA), to achieve 90% recovery of carbon dioxide (CO_2) while requiring reboiler duties ≤2.3 GJ/tonne CO_2 for post-combustion capture of CO_2 from coal- and natural gas-derived flue gas. Extended test campaigns are bing performed at approximately 0.5 megawatt-electric (MWe)-equivalent scale for both coal and natural gas to verify its favorable performance characteristics while evaluating the environmental, health, and safety (EH&S) risks of the technology and quantifying its potential to lower the cost of CO_2 capture. Through a previous U.S. Department of Energy (DOE)-funded project (FWP-70924) under the Discovery of Carbon Capture Substance and Systems (DOCCSS) Initiative, EEMPA was validated in laboratory-scale experiments and confirmed as a viable post-combustion capture solvent.

technical goals

- Develop a cost-effective method for synthesizing sufficient quantities of solvent to perform a 0.5 MWe-scale test at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, while evaluating process modifications needed to optimally operate the solvent process.
- Manufacture the solvent and implement equipment modifications at the NCCC.
- Conduct test campaigns with both coal and natural gas flue gas sources and perform techno-economic analyses (TEAs) and an EH&S risk assessment assuming full-scale deployment of the solvent and process at power plants.

technical content

In this project, Electric Power Research Institute (EPRI), along with their partners, are scaling-up and testing the EEMPA solvent, a water-lean single-amine solvent developed by Pacific Northwest National Laboratory (PNNL). The 0.5 MWe-scale testing is being conducted at the NCCC's Pilot Solvent Test Unit (PSTU). This project will verify that EEMPA can capture CO_2 with heat duties lower than advanced aqueous amine solvents, and with low degradation rates when exposed to real flue gas. The tests also serve as a demonstration of several process design elements, including the use of plastic packings and flash regeneration, that can reduce the capital cost of post-combustion capture processes. Knowledge gained from these tests may also benefit other solvent systems.

In Phase I of the project, activities include development of a cheaper solvent synthesis route ($10/kg cost target) and identification and contracting of a solvent manufacturer, test facility process model development, host site planning, and initial TEA and EH&S risk assessment. Phase II activities comprise the manufacture of the solvent (~2,300 gallons) and modification of the PSTU equipment for the engineering-scale test. Raw material procurement, solvent manufacturing, and quality assurance will be performed and solvent product will be delivered to the test facility. Equipment procurement, permitting, and construction will be completed. A test plan will also be developed. Phase III activities include test facility commissioning, separate test campaigns on coal and natural gas flue gases, performance and emissions data collection, data reduction and analysis, and test facility demobilization and solvent removal. The project will conclude with the completion of a final TEA, a final EH&S risk assessment, and an update of the Technology Maturation Plan (TMP).

EEMPA (Figure 1) is formulated as a water-lean single-amine solvent, consisting of less than 10 wt.% water. The major advantage of a water-lean solvent is lower water vaporization during the solvent regeneration step, especially compared to the aqueous amines.

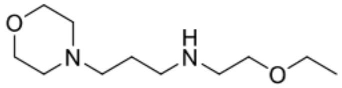

Figure 1: Chemical structure of EEMPA.

This solvent was developed through discrete placement and orientation of hydrogen bonds at the molecular level. The control over hydrogen bond orientation and strength resulted in the development of a derivative that is greater than 90% lower in viscosity than the reference compound. The low regeneration temperature of EEMPA provides a solvent system with potential for a minimal temperature swing between absorption and regeneration cycles.

In previous lab- and bench-scale testing, EEMPA achieved a 90% capture rate with low specific reboiler duties. The favorable thermal performance is attributable to the low water content (around 2 wt.% or less) and a shift in the ionic character of the solvent with higher temperature, disfavoring the CO_2-bound ionic species. Specific reboiler duties down to 2.0 GJ/tonne CO_2 have been observed in experiments. Cost-optimal designs for coal indicate 2.34 GJ/tonne is achievable.

Although EEMPA is formulated without the water of conventional CO_2 capture solvents, it can be used within a conventional solvent scrubbing process design using packed absorption and stripping columns (Figure 2). High viscosity can be an issue for some water-lean candidates; however, EEMPA has demonstrated only modest increases in the viscosity upon uptake of CO_2 (<12 cP at 40°C, 0.22 mol CO_2/mol EEMPA) and mass transfer coefficients are comparable to other solvents. EEMPA can use conventional “simple” stripper designs, but because of the nature of its thermodynamic properties, it may be able to take advantage of alternative designs with simpler construction and lower capital costs. Some of these improvements will be tested at the NCCC.

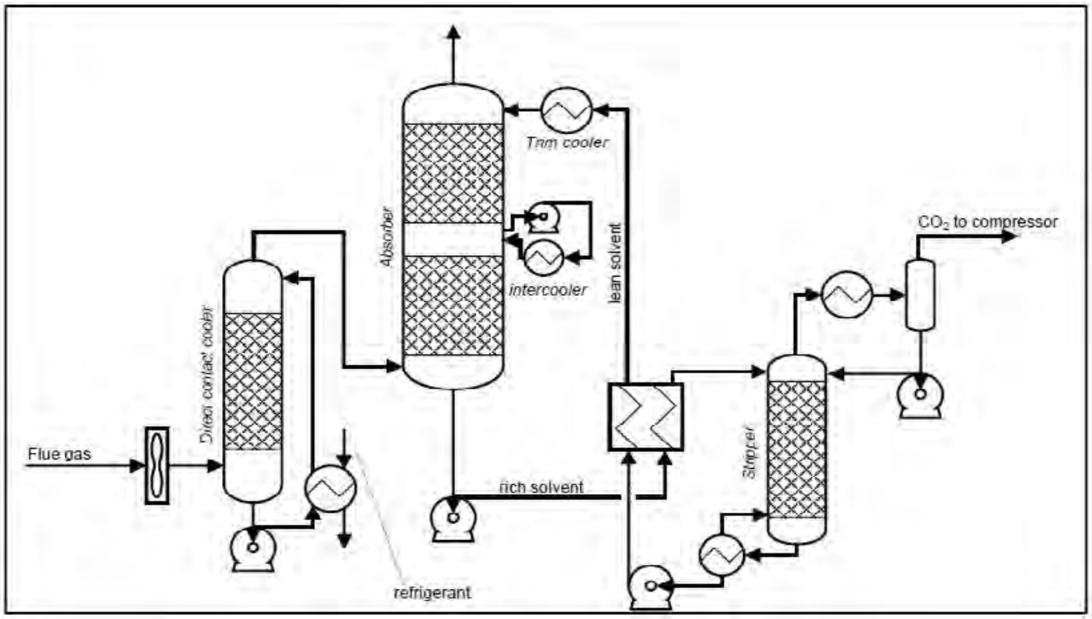

Figure 2: Process flowsheet using a simple stripper arrangement for EEMPA.

Modeling and TEA studies have also estimated 17% lower total equivalent work and 14% lower costs than the National Energy Technology Laboratory’s (NETL’s) Baseline Study Case B12B (Cansolv), and costs as low as $39.4/tonne CO_2 in 2018 pricing basis.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	—
Normal Boiling Point	°C	181.0	—
Normal Freezing Point	°C	<0	—
Vapor Pressure @ 15°C	bar	5E-5	—
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	—
Specific Gravity (15°C/15°C)	-	0.94	—
Specific Heat Capacity @ STP	kJ/kg-K	1.97	—
Viscosity @ 15°C	cP	12	—
Absorption			
Pressure	bar	1	—
Temperature	°C	45	—
Equilibrium CO_2 Loading	mol/mol	0.225	—
Heat of Absorption	kJ/mol CO_2	75	—
Solution Viscosity	cP	25	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	118	—
Equilibrium CO_2 Loading	mol/mol	0.045	—
Heat of Desorption	kJ/mol CO_2	75	—

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., a monoethanolamine [MEA]-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – EEMPA appears to be relatively stable toward oxidative and thermal degradation and hydrolysis in the absence of steel, while sulfur oxide (SO_X) and nitrogen oxide (NO_X) form heat-stable salts.

Solvent Foaming Tendency – EEMPA showed no evidence of foaming during 40 continuous hours of testing with simulated flue gas.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO_2) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively.

Solvent Makeup Requirements – Solvent makeup rates are expected to be at worst comparable to 5M MEA, though preliminary degradation studies indicate higher chemical durability of EEMPA under absorber and stripper conditions.

Waste Streams Generated – Sulfur oxides and NO_X form heat-stable salts, which will need treatment to recover EEMPA in a working process. Preliminary results indicate the addition of polarity-swing assisted regeneration can facilitate regeneration of heat-stable salts, releasing NO_X and SO_X from EEMPA at 60°C and 130°C, respectively.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	39.4	37.9
Cost of Carbon Avoided	\$/tonne CO_2	60.2	58.3
Capital Expenditures	\$/MW	4,231,000	4,231,000
Operating Expenditures	\$/MWhr	28.4	27.2
Cost of Electricity	\$/MWhr	105.7	104.4

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per MW of power generation capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced. Operating costs include both variable operating cost and fixed operating costs at an 85% capacity factor.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Values presented are based on a new build supercritical pulverized coal plant with EEMPA-based post-combustion capture at 90% recovery of CO_2. The base power plant design and TEA referenced Cases B12A/B12B provided by NETL, found in Revision 4 of the “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity” report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*).

Scale of Validation of Technology Used in TEA – The models used to perform the TEA were validated with large bench-scale testing of the solvent in an integrated continuous flow system.

Qualifying Information or Assumptions – The capture process was a "simple stripping" design with a conventional packed regenerator column and steam-driven reboiler.

technology advantages

- Significantly lower regeneration energy compared to aqueous amines.
- Single-component, miscible in water.
- Low viscosity gain upon reaction with CO_2.
- Low surface tension.
- Compatible with potentially cheaper materials of construction (e.g., plastics).
- Low corrosivity.
- Good thermal and chemical stability.
- Potential for advanced heat integration and regeneration steps that could save costs (e.g., flash regeneration).

R&D challenges

- Potentially costly, and large-scale production yet to be demonstrated.
- Imposes need for careful control of the process water balance.

status

The initial TMP, EH&S risk assessment, and TEA were completed. The project team continues finalization of the best route for solvent production at larger scale. Four alternate synthetic routes were investigated with detailed efforts to identify scalable processes with high conversion rates and lower cost raw materials. In identifying modifications needed to the NCCC's facility to host the EEMPA engineering-scale test, Aspen Plus models' development and verification continues to predict performance in the PSTU equipment. The development of plans and equipment specifications is being finalized for the heat exchanger and chiller for the cooler-condenser, plastic packing for the absorber, and flash regeneration using the existing Advanced Flash Stripper equipment. The project team continues communication with the NCCC concerning updating the design hazard review and required permits. EPRI, Southern Company Services, and PNNL have executed their multi-party nondisclosure agreement.

available reports/technical papers/presentations

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," 2021 NETL Carbon Management Research Project Review Meeting, August 12, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Swisher.pdf*

"Engineering-Scale Test of a Water-Lean Solvent for Post-Combustion Capture," DOE Project Kickoff Meeting, April 12, 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11031&filename=Engineering-Scale+Test+of+a+Water-Lean+Solvent+for+Post-Combustion+Capture.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," NETL CO_2 Capture Technology Meeting, August 13, 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," DOE Project Kickoff Meeting, September 15, 2017. *https://www.netl.doe.gov/sites/default/files/netl-file/FWP-70924-PNNL-DOCCSS-kickoff.pdf*.

D. Malhotra, D. C. Cantu, P. K. Koech, D. J. Heldebrant, A. Karkamkar, F. Zheng, M. D. Bearden, R. Rousseau, and V. A. Glezakou, "Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO_2 Capture." ACS Sustainable Chem. Eng., (2019), 7 (8), pp 7535–7542.

D. Malhotra, J. P. Page, M. E. Bowden, A. Karkamkar, D. J. Heldebrant, V. A. Glezakou, R. Rousseau, P. K. Koech. “Phase change aminopyridines as carbon dioxide capture solvents.” Ind. Eng. Chem. Res., (2017), 56, (26), 7534-7540.

D. Malhotra, P. K. Koech, D. J. Heldebrant, D. C. Cantu, F. Zheng, V. A. Glezakou, R. Rousseau, “Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO_2BOLs) for flue gas clean up.” ChemSusChem. (2017), 10, 636 –642.

Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas

primary project goal

ION Clean Energy Inc. (ION) is empirically validating the low capital and operating costs for ION's transformational solvent with revolutionary stability technology (ICE-31) on a 1-megawatt-electric (MWe) slipstream of flue gas from Calpine's Los Medanos Energy Center (LMEC), a commercially dispatched natural gas combined cycle (NGCC) power plant. To accomplish this, the project team is designing, constructing, and operating an engineering-scale carbon dioxide (CO_2) capture pilot that will capture 10 tonnes per day (tpd) of CO_2.

technical goals

- Validate process models on NGCC flue gas over a range of capture efficiencies (up to 99%).
- Demonstrate the exceptional solvent stability of the ICE-31 technology over a long-term operational period to determine true long-term operating costs, including solvent makeup, reclaiming, and disposal.
- Demonstrate expected capital cost savings on NGCC flue gas as compared to baseline technologies.
- Establish true long-term operating costs, including solvent makeup, reclaiming, and disposal.
- Perform an environmental, health, and safety (EH&S) assessment and a techno-economic assessment (TEA).

technical content

The 1-MWe CO_2 capture pilot project leverages the benefits of ION's innovative ICE-31 solvent technology to make a transformational reduction in the levelized cost of electricity while significantly limiting CO_2 emissions from natural gas-fired power plants. The project builds on ION's successful and extensive lab-, bench-, and small pilot-scale testing of solvent technologies and serves as a vital step of piloting a process with actual NGCC flue gas to further validate this technology's expected suitability for future commercial-scale deployment.

In a previous screening of both commercially available amines and designer amines, ION identified the transformational, water-lean amine-based solvent technology ICE-31. ICE-31 exhibits superior regeneration energy, working capacity, kinetics, material compatibility, stability under both oxidative and thermally challenging environments, and a minimal environmental impact.

Under the previous U.S. Department of Energy (DOE)-funded project FE0031727, "Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Project Apollo)," ICE-31 was scaled up and validated at the National Carbon Capture Center's (NCCC) 0.6-MWe pilot solvent test unit on natural gas-fired boiler and coal-fired flue gas; this testing encompassed CO_2 inlet

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Water-Lean Amine-Based Solvent for Natural Gas Applications

participant:
ION Clean Energy Inc.

project number:
FE0031950

predecessor project:
FE0031727

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principal investigator:
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ION Clean Energy Inc.
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partners:
Koch Modular Process Systems; Sargent & Lundy; Calpine Corporation

start date:
10.01.2020

percent complete:
45%

concentrations ranging from 4.4% (simulated NGCC conditions) through 13% (real coal-fired flue gas).

In this project (Project Enterprise), ION will utilize a modular design and fabrication approach to deliver the engineering-scale system that will be designed to yield a CO_2 product flow with greater than 95% purity suitable for compression and dehydration into a CO_2 pipeline. The CO_2 capture process will be optimized to take full advantage of the benefits provided by the ICE-31 solvent in combination with other process improvements, all of which are derived through a process-intensification design philosophy focused on NGCC flue gas. The benefits of this holistic approach include a smaller physical plant, reduced energy requirements, improved CO_2 product quality, less solvent degradation, lower emissions, lower water usage, less maintenance, and lower capital costs.

The long-term test campaign will include a demonstration of end-to-end process optimization; comprehensive chemical costs of the NGCC carbon capture facility; and further validation of ION's rigorous, rate-based process model on NGCC flue gas. Upon completion of this project, ION's solvent technology will be ready for commercial deployment as defined in the Technology Maturation Plan. Learnings from the completed testing under FE0031727 have provided substantial information to support ICE-31's readiness for front-end engineering design for commercial facilities and Project Enterprise seeks to confirm these results and provide any critical operating expenses (OPEX) considerations as projects move to Final Investment Decision.

ION worked with Calpine's LMEC facility to determine the best location for the 1-MWe pilot and identified an optimal location next to the cooling towers (Figure 1). The image shows the proposed location of the pilot system, as well as tie-in points for steam, electricity, cooling water, instrument air, and natural gas (if needed). Additional project team members include Koch Modular Process Systems, a commercial design and fabricator of modular CO_2 capture units who will design and supply the engineering-scale system, and Sargent & Lundy, an experienced engineering firm in the power industry who will manage all balance of plant (BOP) engineering and construction required for site preparation and installation of the pilot system.

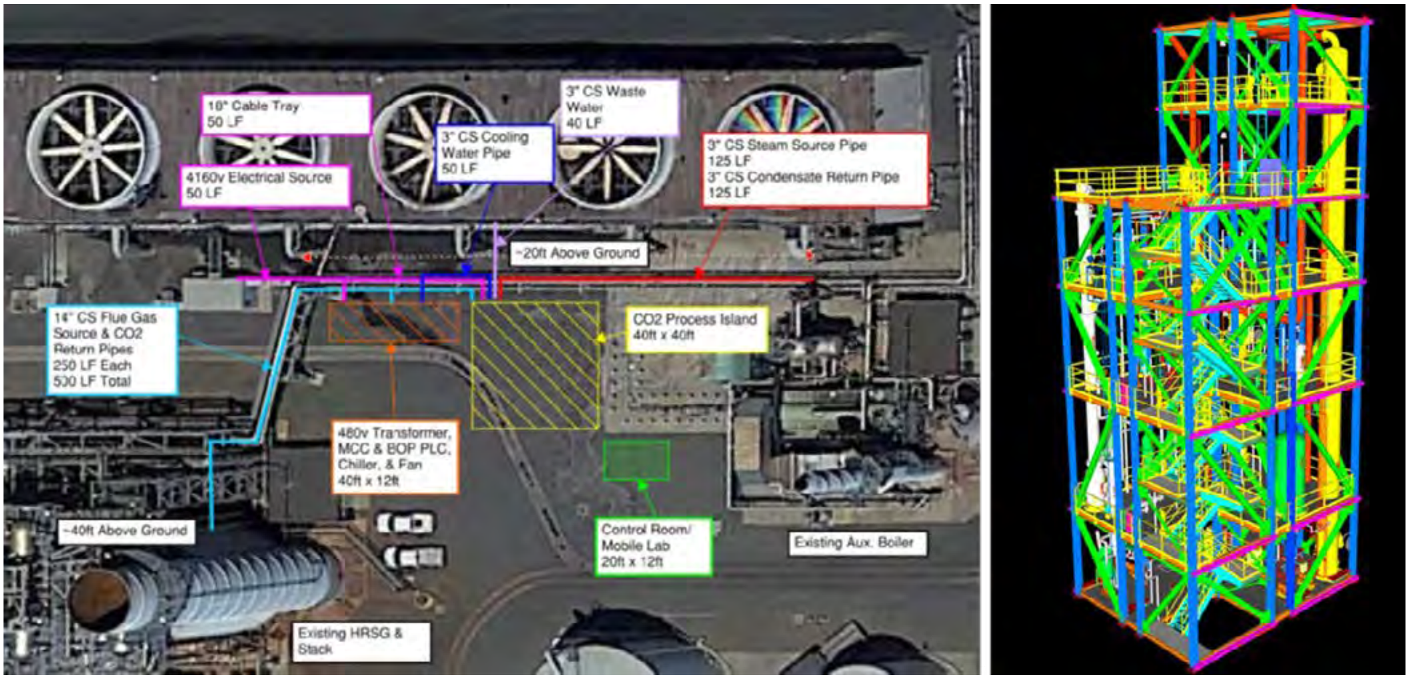

Figure 1: (Left) Overhead view of LMEC with 1,600-ft^2 (150 m^2) pilot site and required tie-ins identified. (Right) Image of the 3D model of the modular system.

Project activities will be accomplished through three phases: design, construction, and operation. The Design Phase will result in a pilot system design that has the necessary flexibility for solvent performance optimization and demonstration. The project team will design the CO_2 capture system and the BOP systems needed to support the 1-MWe pilot at the NGCC facility. A hazard and operability analysis (HAZOP) will be conducted for the pilot system, which will help shape the detailed design. The Construction Phase will realize both the CO_2 capture island and BOP designs and result in a completely assembled system. It will include procurement of necessary equipment and materials, building of the BOP and CO_2 capture systems, and development of the control software. This phase concludes with the installation of the pilot system at the site, the necessary site tie-ins, and site-acceptance testing.

The Operational Phase will commence with baseline testing using first- and second-generation solvents before parametric and long-term testing of ICE-31. The test plan will involve the same baseline parametric testing performed on the previous solvents for a direct comparison, before moving on to a long-term testing strategy to evaluate the solvent lifetime under continuous cycling of operations required to follow the NGCC system. The long-term test campaign will include demonstration of end-to-end process optimization, as well as produce comprehensive technology costs of the NGCC carbon capture facility. The purpose of this long-term testing is to evaluate the solvent performance for a long enough duration to fully understand the interactions and degradation pathways when interacting with the flue gas. This phase will conclude with the decommissioning of the plant and the reversion of the site to its prior state.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	80–150	100–150
Normal Boiling Point	°C	220–250	220–250
Normal Freezing Point	°C	<-15	<-20
Vapor Pressure @ 15°C	bar	<0.0001	<0.0001
Manufacturing Cost for Solvent	$/kg	Proprietary	Proprietary
Working Solution			
Concentration	kg/kg	650–800	650–800
Specific Gravity (15°C/15°C)	-	0.8–1.1	0.8–1.1
Specific Heat Capacity @ STP	kJ/kg-K	1.5–2.5	1.3–2.0
Viscosity @ STP	cP	<10	<10
Surface Tension @ STP	dyn/cm	<50	<50
Absorption			
Pressure	bar	1.0	1.0
Temperature	°C	40	40
Equilibrium CO_2 Loading	gmol CO_2/kg	0.5–1.0	0.5–1.0
Heat of Absorption	kJ/kg CO_2	-1,600 to -1,750	-1,600 to -1,750
Solution Viscosity	cP	<20	<20
Desorption			
Pressure	bar	1.5–2.0	1.5–4.5
Temperature	°C	110–125	110–140
Equilibrium CO_2 Loading	gmol CO_2/kg	0.05–0.20	0.05–0.20
Heat of Desorption	kJ/kg CO_2	<1,800	<1,800

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization unit (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Solvent Contaminant Resistance – Sulfur oxide (SO_x) and nitrogen oxide (NO_x) are manageable. Extremely stable towards oxygen (O_2).

Solvent Foaming Tendency – No issues (more than 3,000 hours experience).

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

Solvent Makeup Requirements – Aimed at less than 0.010 kg/tCO_2.

Waste Streams Generated – Similar profile but estimated to be less than other stable amine-based solvents.

Process Design Concept – Similar to stable amine-based solvents, just a smaller footprint.

Proposed Module Design – N/A.

technology advantages

- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.
- Environmentally benign (i.e., low parasitic load, near-zero emissions, and negligible solvent makeup).
- Low thermal and oxidative degradation rates result in revolutionary solvent stability, reducing solvent makeup rates and associated OPEX.
- Low specific reboiler duty (SRD) and solvent stability result in smaller capture plant equipment, reducing capital expenditure (CAPEX).
- ICE-31 solvent is currently available from commercial chemical manufacturers.

R&D challenges

- Acquiring sufficient long-term solvent performance on natural gas-fired flue gas from a commercially dispatched power station.
- Developing a robust test plan to investigate the necessary conditions required for commercial operations.

status

The project team completed the process design package, updated modular pilot system cost estimate with detailed engineering of the CO_2 island and necessary BOP integration systems. All permit applications were submitted, with favorable results expected as ION's solvent and process mitigate hazardous emissions. For host site preparations, the project team continued meetings to coordinate with the host site for pilot fabrication, updating design criteria, identifying tie-in locations, supporting the modular delivery study, updating the system-level electrical load list, and engaging the general contractor. The modular pilot system will go into fabrication in late Q2 2022, with expected installation in Q4 2022.

available reports/technical papers/presentations

"Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas (Project Enterprise)," DOE Project Kickoff Meeting, December 9, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11039&filename=Engineering-Scale+Demonstration+of+Transformational+Solvent+on+NGCC+Flue+Gas+(Project+Enterprise).pdf*.

"Engineering-Scale Demonstration of Transformational Solvent on NGCC Flue Gas (Project Enterprise)," 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Fine_0.pdf*

"Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Apollo)," 2021 NETL Carbon Management Research Project Review Meeting, August 12, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Fine.pdf*

Sorbent-Based Post-Combustion CO_2 Slipstream Testing

primary project goal

TDA Research Inc. is designing, constructing, and operating a slipstream 0.5-megawatt-electric (MWe) pilot-scale process for post-combustion carbon dioxide (CO_2) capture using their low-cost alkalized alumina sorbent to conduct parametric and long-term steady-state testing to demonstrate the effectiveness of the technology to reduce the cost of CO_2 capture and to develop scale-up conditions for the process.

technical goals

- Modify bench-scale unit to mimic proposed pilot plant configuration and conduct testing in bench unit to optimize process and collect data for pilot plant design.
- Characterize breakthrough performance and pressure drop for different sorbent pellet sizes.
- Design pilot plant unit based on developed low-cost alkalized alumina sorbent technology.
- Scale-up production of sorbent.
- Fabricate and install pilot plant unit at the National Carbon Capture Center (NCCC).
- Perform parametric and steady-state testing on pilot plant using actual flue gas.
- Update environment, health, and safety (EH&S) study and techno-economic analysis (TEA) based on pilot plant testing results.

technical content

TDA Research Inc. is designing, constructing, and operating a slipstream 0.5-MWe pilot-scale process for post-combustion CO_2 capture. This technology is based on their novel dry alkalized alumina sorbent developed previously in a U.S. Department of Energy (DOE)-funded project (DE-NT0005497). The regenerable sorbent acts as a physical adsorbent for CO_2. The CO_2 capture process runs near isothermally at around 140–150°C in both adsorption and regeneration, requiring no heating or cooling between adsorption and regeneration steps. The sorbent is regenerated with low pressure (15.5 pounds per square inch absolute [psia]) steam. The sorbent shows excellent tolerance to contaminants, including sulfur dioxide (SO_2) and nitrogen oxides (NO_X).

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the adsorber/regenerator unit and (2) the CO_2 compression and purification unit. The process is designed for the sorbent to remove the CO_2 from the flue gas at intermediate temperature and near-ambient pressure, and then be regenerated with low-pressure superheated steam. A multiple fixed-bed design is used, providing counter-flow contact between solids and gases, where the beds cycle between adsorption and desorption. The flue gas flows in parallel through the adsorption beds and in series across regeneration beds. This setup has several advantages over moving beds, including a simple-

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Alkalized Alumina Sorbent Pilot Test

participant:
TDA Research Inc.

project number:
FE0012870

predecessor projects:
NT0005497

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partners:
University of California at Irvine; Porocel; Babcock and Wilcox; Louisiana State University; Western Research Institute; ExxonMobil; National Carbon Capture Center

start date:
02.03.2014

percent complete:
95%

bed design, basic ductwork, low construction cost, and the elimination of parasitic power required to move the sorbent, all of which result in a lower overall cost than moving beds.

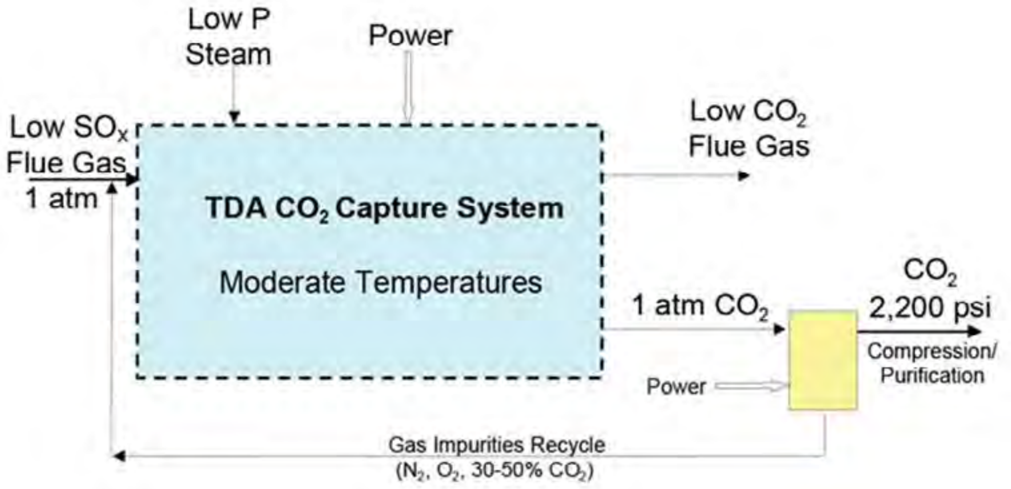

Figure 1: Block flow diagram of TDA's CO_2 capture system.

The process scheme was optimized through testing with sorbent loaded in a 10-bed bench-scale unit. Operating in split steam saver (SS) mode to reduce the need for fresh regeneration steam resulted in improved capture performance. TDA evaluated several different sorbents, including commercial and customized sorbents, on the bench-scale unit to determine an optimal sorbent for testing at the NCCC.

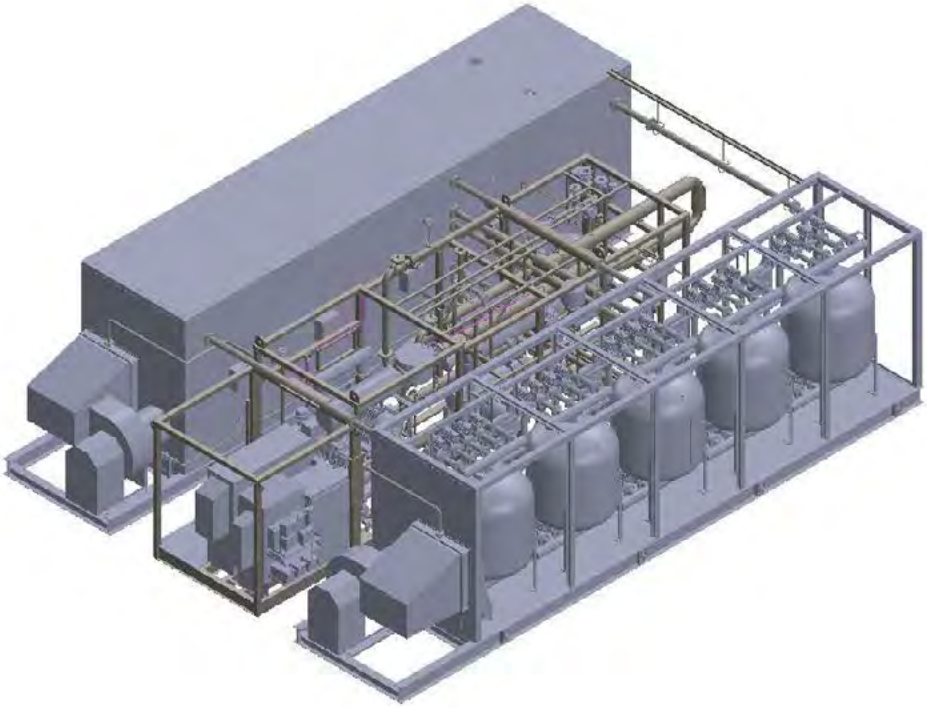

Figure 2: TDA's 0.5-MWe test skid.

The slipstream pilot plant is a 0.5-MWe skid-mounted system (shown in Figure 2) with two sorbent bed trailers, each housing five sorbent beds. Each trailer is insulated and heated to provide an isothermal environment. The adsorber/regeneration system containing multiple fixed beds with alumina sorbent switches between adsorption, regeneration, and purge operations. The complete slipstream pilot unit includes adsorber/regeneration beds, heat exchangers, blowers, valving, and instrumentation.

Slipstream pilot unit testing under both parametric and steady-state conditions using actual coal-fired and natural gas flue gases provides data and recommended operating conditions to update the TEA and EH&S assessment, as well as for definition of recommended scale-up conditions. The project aims to demonstrate the novel system for reduction in carbon capture cost.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1320	750
Bulk Density	kg/m^3	790	520
Average Particle Diameter	mm	1.5	3.175
Particle Void Fraction	m^3/m^3	0.40	0.55
Packing Density	m^2/m^3	9.4E+07	9.4E+07
Solid Heat Capacity @ STP	kJ/kg-K	0.72	0.72
Crush Strength	kg$_f$	8	8
Manufacturing Cost for Sorbent	\$/kg	6.5	3
Adsorption			
Pressure	bar	1.12	1.12
Temperature	°C	140	140
Equilibrium Loading	g mol CO_2/kg	1.0	1.5
Heat of Adsorption	kJ/mol CO_2	-12.5 to -41.9	-12.5 to -41.9
Desorption			
Pressure	bar	1.17	1.17
Temperature	°C	150	150
Equilibrium CO_2 Loading	g mol CO_2/kg	0.93	1.0
Heat of Desorption	kJ/mol CO_2	12.5 to 41.9	12.5 to 41.9
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Simulated moving bed	
Flue Gas Flowrate	kg/hr	2,273	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 1.013	
Adsorber Pressure Drop	bar	0.02	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent is an adsorbent and is regenerated with steam.

Sorbent Contaminant Resistance – Based on extended cycling 1,500 hours with simulated flue gas with 13.8% CO_2, 104 parts per million (ppm) SO_2, 3% oxygen (O_2), and 9% water (H_2O), sorbent life was calculated to be one year with 5 ppm of SO_2. No effect of NO_x on capacity was seen after 200 cycles with 739 ppm nitric oxide (NO) and 84 ppm nitrogen dioxide (NO_2).

Sorbent Attrition and Thermal/Hydrothermal Stability – None provided.

Flue Gas Pretreatment Requirements – Flue gas should have <5 ppm sulfur oxides (SO_x).

Sorbent Makeup Requirements – 15% per year.

Waste Streams Generated – None known.

Process Design Concept – See Figure 1 above.

Proposed Module Design – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module. TDA's CO_2 capture system is located downstream of the FGD unit. The adsorbent removes dilute CO_2 from the flue gas (10 to 14% CO_2, 8 to 10% H_2O, <5 ppm SO_2) at intermediate temperature (140°C) and near-ambient pressure.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.90	40.0
Cost of Carbon Avoided	\$/tonne CO_2	47.65	—
Capital Expenditures	\$/MWhr	52.0	—
Operating Expenditures	\$/MWhr	40.2	—
Cost of Electricity	\$/MWhr	92.2	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The analysis was based on Case 12 in "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 2."

Scale of Validation of Technology Used in TEA – The analysis was based on pilot-scale testing.

technology advantages

- Inexpensive, durable sorbent.
- Low-pressure (17 psi) steam for sorbent regeneration, low regeneration energy.
- Near isothermal operation.
- No heat recovery from solids required.
- Rapid adsorption/regeneration kinetics due to surface-only adsorption.
- Low heat of adsorption.
- Counter-current operation maximizes capture efficiency and sorbent loading.

R&D challenges

- Minimize the parasitic demands from the sorbent system.
- Effectively produce a sorbent from low-cost raw materials with extensive regenerative life.

status

TDA Research Inc. has designed and constructed the 0.5-MWe-scale pilot plant test unit and produced the sorbent needed for testing. The skid has been installed at the NCCC for parametric and long-term testing. Parametric tests were completed with actual coal flue gas and simulated natural gas flue gas (coal flue gas diluted with air). High-purity CO_2 product (greater than 95%) was achieved by tuning a process step that diverts a small fraction of the product stream when a bed first comes onto regeneration. Long-term testing was completed, with 90% capture and 95% CO_2 purity maintained throughout the test by adjusting operating parameters.

available reports/technical papers/presentations

Elliott, J. and Yi, F. "Pilot Unit Testing at NCCC of Sorbent-based CO_2 Capture Project # DE-FE0012870," presented at 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting – Point Source Capture – Lab, Bench, and Pilot-Scale Research, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Elliott.pdf*.

Elliott, J. and Yi, F. "Pilot Unit Testing at NCCC of Sorbent-based CO_2 Capture Project # DE-FE0012870," presented at 2020 NETL Integrated Project Review Meeting-Carbon Capture, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Elliott.pdf*.

Elliott, J. and Yi, F. "Update on Pilot Unit of Sorbent Based Post-Combustion CO_2 Capture," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Elliott-TDA-Sorbent-CO2-Capture.pdf*.

Elliott, J. and Yi, F. "Update on Pilot Unit of Sorbent Based Post-Combustion CO_2 Capture," Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Elliott-TDAR-Pilot-Unit-Sorbent-Based-Capture.pdf*.

Elliott, J. and Yi, F. “Sorbent Based Post-Combustion CO_2 Slipstream Testing,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/J-Elliott-TDA-Post-Combustion-CO2-Slipstream-Testing.pdf*.

Elliott, J., “Post-Combustion CO_2 Capture with Low Cost Solid Sorbent Slipstream Testing,” Presented at 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/2-Tuesday/J-Elliott-TDA-Slipstream-Test-of-Sorbent-Based-Capture.pdf*.

Elliott, J. and Copeland, B. “Sorbent Based Post-Combustion CO_2 Slipstream Testing,” Presented at 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://netl.doe.gov/sites/default/files/event-proceedings/2015/co2captureproceedings/J-Elliot-TDA-Sorbent-Slipstream-Testing.pdf*.

Elliott, J., et al. “Sorbent Based Post-Combustion CO_2 Slipstream Testing,” Presented at 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://netl.doe.gov/sites/default/files/event-proceedings/2014/2014%20NETL%20CO2%20Capture/J-Elliot-TDA-Sorbent-Based-Post-Combustion-CO2-Slip-Stream.pdf*.

Chevron Natural Gas Carbon Capture Technology Testing Project

primary project goal

Chevron, partnering with Svante Inc., Electricore Inc., Kiewit Engineering Group Inc., Kiewit Power Constructors, and Offshore Technical Services, is validating the transformational VeloxoTherm™ solid sorbent carbon capture technology at engineering scale under indicative natural gas flue gas conditions and continuous long-term operation at Chevron's Kern River Oil Field. The VeloxoTherm technology uses proprietary novel CALgary Framework-20 (CALF-20) metal-organic framework (MOF) sorbent materials and is comprised of a rotary adsorption machine for rapid-cycle thermal swing adsorption (RC-TSA) using structured adsorbent beds. The team is designing, constructing, and testing an engineering-scale plant of approximately 25 tonnes per day (TPD) under steady-state conditions at varying flue gas carbon dioxide (CO_2) concentrations (4–14%) using a once-through-steam-generator (OTSG). Chevron is also conducting a techno-economic analysis (TEA) on the VeloxoTherm technology integrated into a full-scale natural gas combined cycle (NGCC) power plant, as well as a comprehensive gap analysis.

technical goals

- Successfully complete the design, construction, commissioning, and long-term testing of an engineering-scale plant of approximately 25 TPD under steady-state conditions.
- Conduct a TEA on the Svante RC-TSA technology as integrated into a nominal 550-megawatt (MW) (net) natural gas power plant.
- Conduct a comprehensive gap analysis addressing the current stage of development of the Svante technology for NGCC application, and summarize the research, development, and demonstration requirements to close any of the gaps to approach achievement of the U.S. Department of Energy's (DOE) Carbon Capture Program performance goal of CO_2 capture with 95% CO_2 purity at a cost of $30/tonne of CO_2 captured by 2030.
- Complete a Technology Maturation Plan (TMP) and Environment, Health, and Safety (EH&S) Risk Assessment.

technical content

The VeloxoTherm process developed by Svante is comprised of an RC-TSA process that uses a patented architecture of structured adsorbent beds (SABs) and a novel process design and embodiment to capture CO_2 from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties that serve to greatly improve the performance of gas separation, enabling fast cycle times and small equipment sizes that deliver attractive capture economics. Figure 1 shows the Rotary Adsorption Machine (RAM) design at the core of the technology. Svante uses solid adsorbents that have very high surface-to-volume ratios, instead of liquid chemicals (amines or potassium hydroxide), to capture CO_2. A new class of advanced sorbent materials, CALF-20, has been developed by Svante and lab-tested under DOE Cooperative Agreement No. DE-FE0031732 and field-tested in Q3-2020 at a cement plant in Vancouver, Canada.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent

participant:
Chevron

project number:
FE0031944

predecessor projects:
N/A

NETL project manager:
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Juan Gou
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juangou@chevron.com

partners:
Electricore Inc.; Svante Inc.; Kiewit Engineering Group Inc.; Kiewit Power Constructors; Offshore Technical Services

start date:
10.01.2020

percent complete:
75%

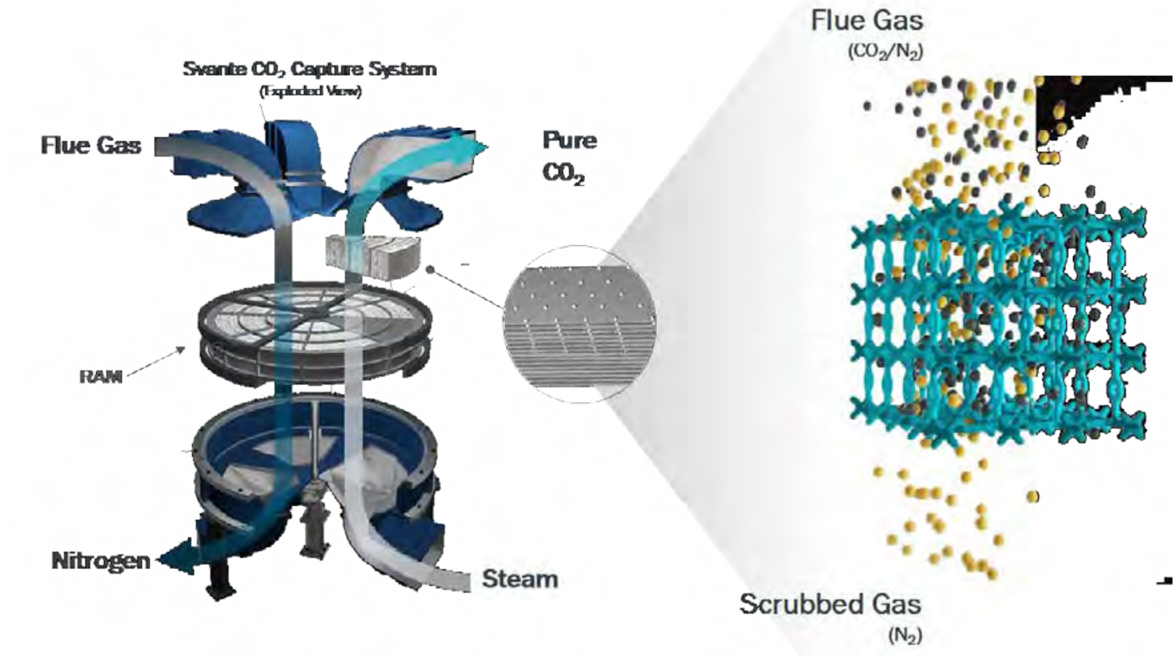

Figure 1: VeloxoTherm™ Rotary Adsorption Machine.

The sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. Utilizing CALF-20 eliminates the need for a site nitrogen generator that is required on an amine-doped silica sorbent plant to protect the adsorbent from oxidation during conditioning steps. The VeloxoTherm process has been scaled-up to 30 TPD of CO_2 and is undergoing demonstration with flue gas derived from natural gas combustion at Cenovus in Canada using a first-generation sorbent material of amine-doped silica. In this proposed project, the team plans to leverage the design and learnings from the Cenovus 30-TPD project to improve the performance and flexibility of a second-of-a-kind (SOAK) engineering-scale plant (400 Series) using CALF-20 MOF sorbent material.

The test program will be performed at a feed CO_2 concentration of approximately 8% (10.5% dry basis) for normal steady-state operations, with flexibility to gather data and test equipment at a wide operating range of 4–14% CO_2 in the feed by employing an air-mixing and CO_2 product recycling system. The CO_2 product specification will be 95% (versus 85% in the Cenovus unit), meeting existing CO_2 pipeline specifications. To achieve this product purity and process flexibility, a reflux step will be added to the RAM and balance of plant (BOP).

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m³	350-380	350-380
Bulk Density	kg/m³	NA	NA
Average Particle Diameter	mm	0.31-0.35	0.31-0.35
Particle Void Fraction	m³/m³	NA	NA
Packing Density	m²/m³	2300-2500	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Thermal Conductivity	W/(m-K)	0.25-0.35	0.25-0.35
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO_2)	g mol CO_2/kg	1.7-1.9	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			

Pressure	bar	0.8-1.0	0.8-1.0
Temperature	°C	120-140	120-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.3-0.4
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design			
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving bed	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95 95 150	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry sorbent measured with 20% CO_2 in N_2 mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional Direct Contact Cooler (DCC).

Sorbent Make-Up Requirements – A three- to five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site specific	Site specific
Capital Expenditures	\$/TPD	70,000 to 80,000	60,000 to 70,000
Operating Expenditures	\$/tonnes CO_2	26 - 28	20-23
Cost of Electricity	\$/tonnes CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5 to 6 cents per kWh.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the TEA from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).
- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.

R&D challenges

- Engineering-scale testing and analysis.

status

Chevron, through its partnership with Svante, completed the Preliminary TEA Summary Report in response to a request for a Class IV TEA of a retrofit package to capture CO_2 from existing NGCC power plant facilities. The project also completed a general process flow diagram identifying all major process equipment for the power plant, including CO_2 capture and compression systems, separation vessels, heat exchangers, pumps, compressors, etc. Chevron's partner Svante upgraded the Rotary Seal Validation Testing (RSVS) for design validation of key parameters that cannot be replicated on the smaller material seal test station. The RSVS upgrade, including design, procurement, assembly, programming, and commissioning, was completed. The RSVS has been upfitted with a new gearbox to enable operation at expected rotational speed, along with true-size seal segments and counterface parts similar to actual RAM seal parts for design validation. A 50-day RSVS was completed. The project also demonstrated sorbent scale-up production required for project execution. Additional and complementary tests conducted at Svante confirm material properties, sorbent characterization, and slurry processability into coated laminates are meeting current specifications developed from Svante internal synthesized materials.

available reports/technical papers/presentations

Justin Freeman, "Chevron Natural Gas Carbon Capture Technology Testing Project," Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11026&filename=Chevron+Natural+Gas+Carbon+Capture+Technology+Testing+Project.pdf*.

Justin Freeman, "Chevron Natural Gas Carbon Capture Technology Testing Project," Budget Period 1 Project Review meeting presentation, Pittsburgh, PA, July 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11028&filename=Chevron+Natural+Gas+Carbon+Capture+Technology+Testing+Project.pdf*.

Justin Freeman, "Chevron Natural Gas Carbon Capture Technology Testing Project," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Freeman.pdf*

Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture

primary project goal

TDA Research, Inc. (TDA) is designing and constructing a 1-megawatt-electric (MWe)-scale membrane-sorbent hybrid post-combustion carbon capture system and evaluating its operation in a long-duration field test using industrial flue gas that closely resembles coal-fired flue gas. Their hybrid process consists of a polymeric membrane and low-temperature physical adsorbent to remove carbon dioxide (CO_2) from flue gas.

technical goals

- Design the 1-MWe-scale test unit.
- Fabricate the test unit.
- Install the test unit at the Technology Centre Mongstad (TCM).
- Complete a nine- to 12-month-long field test campaign at TCM using actual flue gas.
- Complete an updated techno-economic analysis (TEA) based on the field test data.

technical content

TDA is designing, constructing, and operating a slipstream 1-MWe pilot-scale process for post-combustion CO_2 capture using actual flue gas. The hybrid process consists of a polymeric membrane and a low-temperature physical adsorbent. This technology is based on TDA's previously developed sorbent, and a membrane developed by Membrane Technology and Research (MTR). TDA's sorbent uses a mesoporous carbon modified with surface functional groups to remove CO_2 via physical adsorption. Carbon dioxide-surface interaction is strong enough to allow low partial pressure operation and regeneration energy is low because the CO_2 is not bonded to the sorbent. The feasibility of the hybrid sorbent-membrane system was initially proven in a prior U.S. Department of Energy (DOE)-funded project (DE-SC0011885) using coal-derived flue gas at 4-kilowatt-electric (kWe) scale, showing greater than 90% CO_2 capture and high purity.

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the membrane unit and (2) the CO_2 adsorption unit. The membrane operates at approximately 50°C under mild vacuum, removing approximately 50% of the CO_2 and nearly all the water. The reduced vacuum pump requirements reduce power consumption and system cost. The sorbent removes the remaining CO_2 from the membrane effluent to ensure 90% carbon capture. Sorbent regeneration is facilitated using boiler feed air as a sweep gas and the CO_2-laden air after sorbent regeneration is fed to the boiler to generate a CO_2-rich flue gas stream to increase the driving force across the membrane. The overall energy intake of the CO_2 capture process is reduced by using a hybrid membrane-sorbent configuration, while the capture efficiency is not degraded.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Membrane-Sorbent Hybrid System for Coal-Fired Flue Gas

participant:

TDA Research, Inc.

project number:

FE0031603

predecessor projects:

SC0011885

NETL project manager:

Andrew O'Palko
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galptekin@tda.com

partners:

Membrane Technology and Research; Technology Centre Mongstad; Gas Technology Institute; University of California Irvine

start date:

08.15.2018

percent complete:

85%

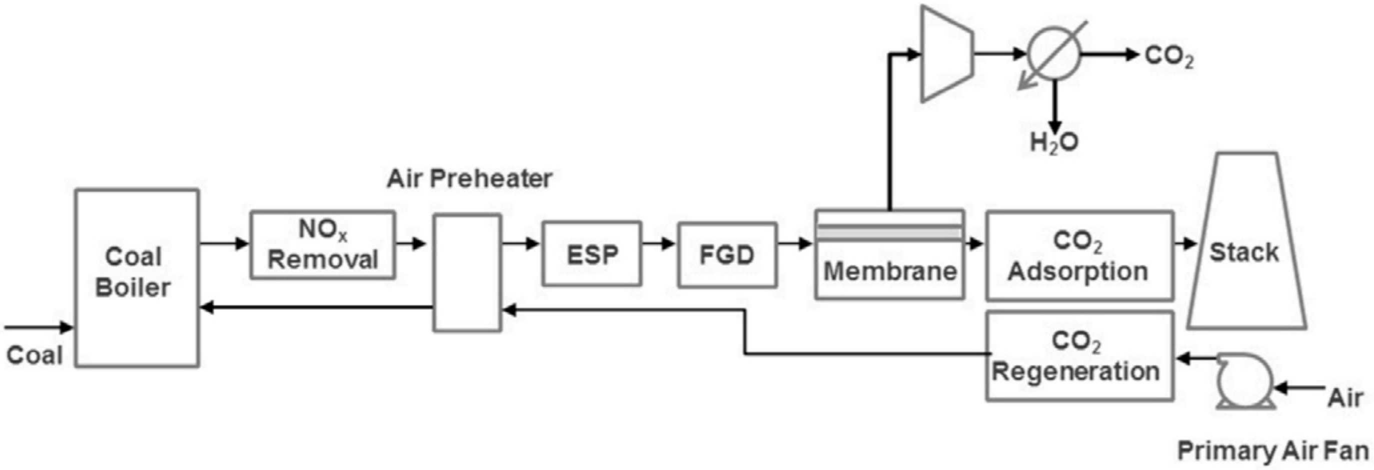

Figure 1: Flow diagram of the TDA Research hybrid membrane-sorbent CO_2 capture system.

TDA is developing its modular sorbent bed concept known as the radial outflow reactor, shown in Figure 2. Two modules would be used, one operating in adsorption and one in desorption, to provide continuous transfer of CO_2 into the boiler air. For the 1-MWe-scale tests at TCM, three modules are used, as shown in Figure 3, with two of the modules operating in series to show the modular design concept works.

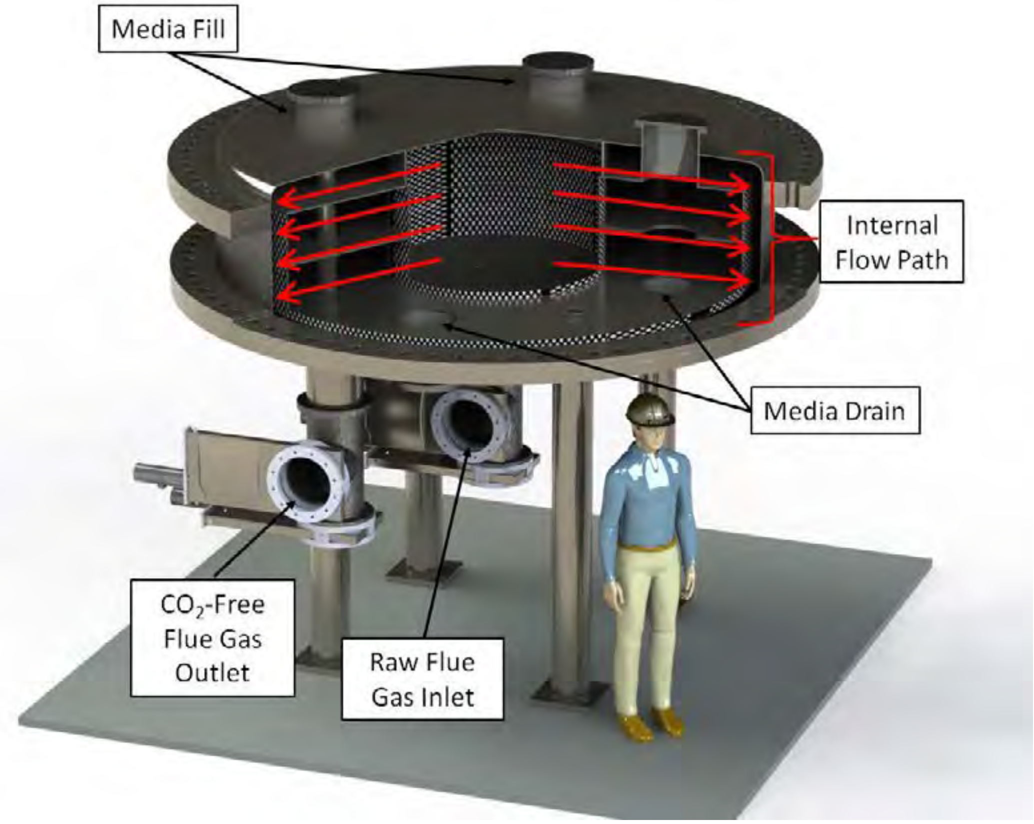

Figure 2: TDA Research's modular radial outflow reactor concept.

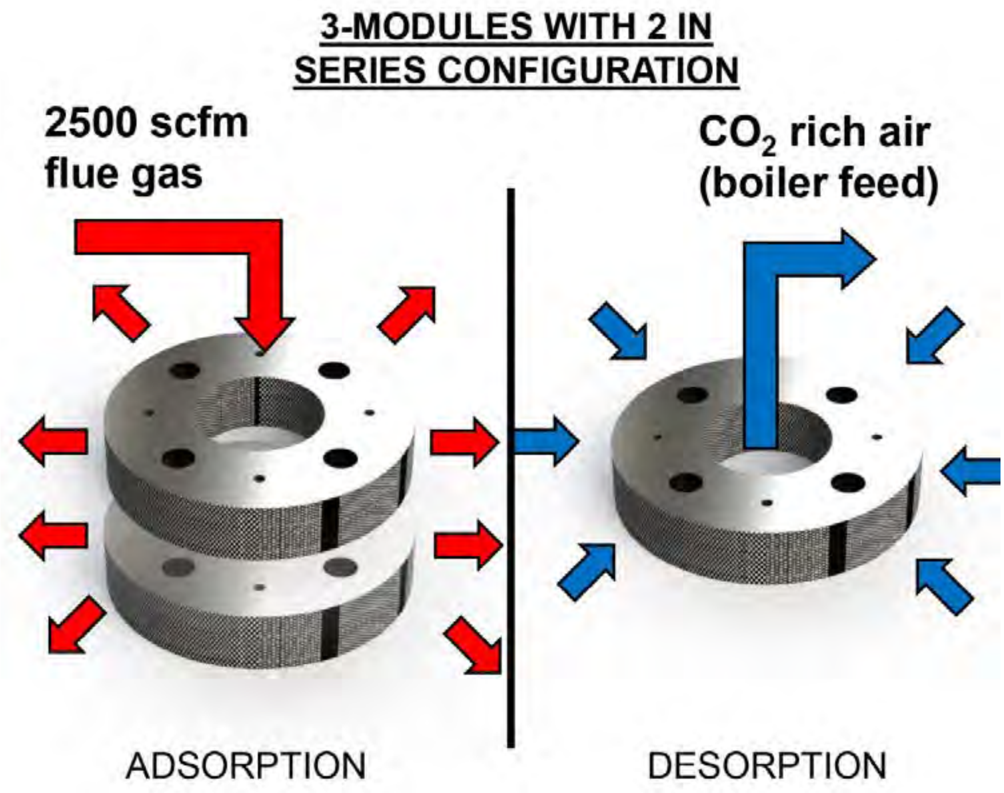

Figure 3: TDA Research 1-MWe modules.

The 1-MWe membrane-sorbent hybrid pilot test unit is being designed and built to be installed for testing at TCM in Norway. A nine- to 12-month test campaign using industrial flue gas that closely resembles coal-fired flue gas is planned to evaluate the operating performance of the capture system at various conditions and to complete at least 6,000 hours of continuous operation. This testing under both parametric and steady-state conditions provides data and recommended operating conditions to update the membrane performance data and the TEA and environment, health, and safety (EH&S) analysis. The project aims to demonstrate the novel hybrid system for reduction in carbon capture cost. The sorbent process parameters are provided in Table 1 and the membrane and process parameters are provided in Table 2.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1300	1300
Bulk Density	kg/m^3	589	589
Average Particle Diameter	mm	0.4-1.7	0.8-2.4[a]
Particle Void Fraction	m^3/m^3	0.37	0.37
Packing Density	m^2/m^3	240	240
Solid Heat Capacity @ STP	kJ/kg-K	0.93[b]	0.93[b]
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	3.75	3.75
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	30	30
Equilibrium Loading	g mol CO_2/kg	0.5	0.5
Heat of Adsorption	kJ/mol CO_2	20-30	20-30
Desorption			

Pressure	bar	1.0		1.0
Temperature	°C	30		30
Equilibrium CO_2 Loading	g mol CO_2/kg	0.05		0.05
Heat of Desorption	kJ/mol CO_2	20-30		20-30
Proposed Module Design		*(for equipment developers)*		
Flow Arrangement/Operation	—		Radial flow fixed beds	
Flue Gas Flowrate	kg/hr		TBD	
CO_2 Recovery, Purity, and Pressure$^+$	% / % / bar	N/A	NA	N/A
Adsorber Pressure Drop	bar		<100 mbar	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		TBD	

$^+$ Sorbent subsystem does only recirculation of CO_2 and is the secondary separation system in the hybrid configuration.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – U.S. Patent No. 9,120,079 B1.

Sorbent Contaminant Resistance – Sulfur oxide (SO_X) and nitrogen oxide (NO_X) tolerant up to 100 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – Less than 0.1% over one year.

Flue Gas Pretreatment Requirements – None.

Sorbent Makeup Requirements – Five-year replacements.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, included above.

Proposed Module Design – Radial flow fixed beds.

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary Polymer	
Materials of Fabrication for Support Layer	—	Proprietary Polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	Thin film composite	Thin film composite
Max Trans-Membrane Pressure	bar	1.0	1.0
Hours Tested without Significant Degradation	—	11,000	3 years
Manufacturing Cost for Membrane Material	$/m^2	—	—
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000 to 3,000	3,000
CO_2/H_2O Selectivity	—	0.25	0.25
CO_2/N_2 Selectivity	—	25-30	30
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Partial countercurrent	
Packing Density	m^2/m^3	500 to 1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	TBD	
CO_2 Recovery, Purity, and Pressure$^+$	%/%/bar	90% 95% 150	
Pressure Drops Shell/Tube Side	bar	0.15	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	TBD	

$^+$ CO_2 recovery, purity, and pressure downstream of the cryogenic purification and pumping system.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – proprietary polymeric membrane

Contaminant Resistance – SO_x and NO_x tolerant up to 100 ppm.

Flue Gas Pretreatment Requirements – None.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

Proposed Module Design – Plate and frame module design for full-scale unit, spiral wound modules used in field test.

technology advantages

- Low pressure drop and high performance at the low CO_2 partial pressure in the adsorption stage.
- Efficient membrane operation due to high driving force and low cost due to mild vacuum requirements.
- Reduced capture cost while maintaining CO_2 capture performance due to the hybridization of the process.
- A preliminary TEA showed a substantial improvement in net plant efficiency (approximately F3.5% increase on higher heating value [HHV] basis) compared with the state-of-the-art amine-based CO_2 capture system.

R&D challenges

- Scaling-up the hybrid system from bench-scale to the 1-MWe system size for testing in this project.
- Assuring high membrane selectivity to get greater than 95% purity CO_2.
- Maintaining uniform flow distribution in sorbent reactor.

status

Most project work has been completed, including the TEA. Design validation and modeling work is underway, which will be followed by a short optimization study and updated TEA.

available reports/technical papers/presentations

Aleptekin, G.; Jayaraman, A.; Bonnema, M.; Bruinsma, D.; Cates, M.; Cesario, M.; Gribble, D.; Gushlaw, B.; Hohman, J.; Kugler, F., 2021, "Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture." Presented at the 2021 Carbon Management and Oil and Gas Research Project Review Meeting. DOE/NETL. Pittsburgh, PA. August 12th. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alpteken.pdf*.

Aleptekin, G.; Jayaraman, A.; Gribble, D.; Cates, M.; Hohman, J.; Kugler, F.; Bruinsma, D., 2020, "Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture." Presented at the DOE/NETL 2020 Carbon Capture Project Review Meeting. Pittsburgh, PA. October 7th. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Alptekin_B.pdf*.

Alptekin, G.; Jayaraman, A.; Gribble, D.; Bonnema, M., 2018, "Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture," Project Kickoff Meeting Presentation, Pittsburgh, PA. October 1st. *https://netl.doe.gov/projects/plp-download.aspx?id=10483&filename=Membrane-Sorbent+Hybrid+System+for+Post-Combustion+CO2+Capture.pdf.*

Alptekin, G., Jayaraman, A.; Gribble, D.; Bonnema, M., 2018, "Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture," Presented at the NETL 2018 CO_2 Capture Technology Meeting, Pittsburgh, PA. August 16th. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDAR-Membrane-Sorbent-Hybrid.pdf*.

Engineering-Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture

primary project goal

Gas Technology Institute (GTI) is advancing the Ohio State University's (OSU) transformational membrane-based carbon dioxide (CO_2) capture technology through engineering-scale testing on actual coal-derived flue gas at the Wyoming Integrated Test Center (ITC). The amine-containing CO_2-selective membranes developed under U.S. Department of Energy (DOE)-funded projects (FE0031731; FE0026919; FE0007632) consist of a thin selective layer coated on a polymer support and exhibit high CO_2 permeance and very high selectivity of CO_2 over nitrogen (N_2). The superior performance is based on a facilitated transport mechanism, in which a reversible CO_2 reaction with fixed-site and mobile amine carriers enhances the CO_2/N_2 separation. The objectives of this project are to fabricate commercial-size membrane modules; design and install a 1-megawatt-electric (MWe) CO_2 capture system at ITC; conduct parametric testing with one- and two-stage membrane processes at varying CO_2 capture rates (60–90%); perform continuous testing at steady-state operation for a minimum of two months; and gather the data necessary for further process scale-up.

technical goals

- Design and build an engineering-scale CO_2 capture system using OSU's transformational membrane in commercial-size membrane modules.
- Conduct tests on coal flue gas at ITC and demonstrate a continuous, steady-state operation for a minimum of two months. Gather the data necessary for process scale-up.
- Complete initial detailed techno-economic analysis (TEA) and detailed design of the engineering-scale system.
- Complete construction of the engineering-scale system and install it at ITC.
- Complete engineering-scale testing and analysis, achieve 95% CO_2 purity, and validate a capture cost of $30/tonne of CO_2 captured and cost of electricity (COE) at least 30% less than DOE baseline approach.

technical content

OSU has developed a transformational membrane in commercial-size—a spiral-wound membrane module shown in Figure 1. The novel CO_2-selective membranes are synthesized by formulating amine-containing polymer into a thin-film composite membrane configuration (Figure 2). The polymer selective layer, typically 100–200-nm thick, carries out the CO_2/N_2 separation. The highly gas-permeable nanoporous support layer provides the mechanical strength necessary for use in a separation module.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Membrane Technology for Coal-Fired Power Plants

participant:

Gas Technology Institute

project number:

FE0031946

predecessor projects:

FE0007632; FE0026919; FE0031731

NETL project manager:

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principal investigator:

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Gas Technology Institute
shiguang.li@gastechnology.org

partners:

Ohio State University;
Trimeric Corporation;
Wyoming Integrated Test Center

start date:

10.01.2020

percent complete:

15%

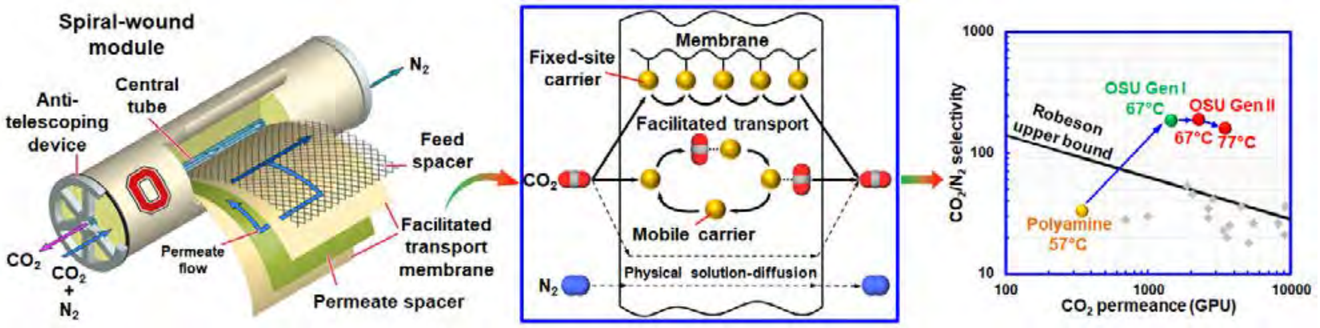

Figure 1: Diagrams of the membrane module (left), transport mechanism (middle), and performance (right).

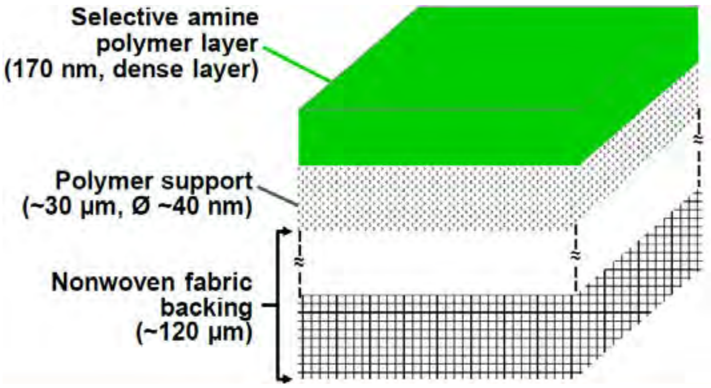

Figure 2: Schematic of the thin-film composite membrane.

In the presence of a transmembrane partial pressure difference, as illustrated in Figure 1 (middle), CO_2 molecules from the feed side dissolve in the selective layer via the reaction with the amine carriers ($CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH^+ + HCO_3^-$). The reaction product (HCO_3^-) diffuses across the membrane and eventually is converted back to the CO_2 molecules via the reverse reaction and released on the low-pressure side.

The fixed-site carrier is covalently bound to the polymer, and the mobile carrier exists as nonvolatile amino acid salt. Thus, the carriers stay in the membrane. The permeation of N_2 is extremely slow due to the lack of reactive diffusion. The disparate permeation rates result in a high CO_2 permeability and a high CO_2/N_2 selectivity, which are usually more than three-fold of those shown by membranes relying on size or condensability discrimination through the solution-diffusion mechanism.

The project is to design and build a nominal 1-MWe engineering-scale unit (approximately 20 tonnes per day [TPD]) using this transformational membrane with commercial-size modules and test it with coal-fired flue gases at ITC, located at Basin Electric Power Cooperative's Dry Fork Station, seven miles north of Gillette, Wyoming. The testing goal is to capture 60–90% CO_2 of the feed CO_2 with approximately 95% CO_2 purity. The test system will proceed in two modes—a single-stage process that is anticipated to be preferred for the lower CO_2 capture rates and an innovative retentate recycle two-stage process for the higher CO_2 capture rates (Figure 3). The data will be used in the TEA to determine the optimum configuration to meet DOE's programmatic goals.

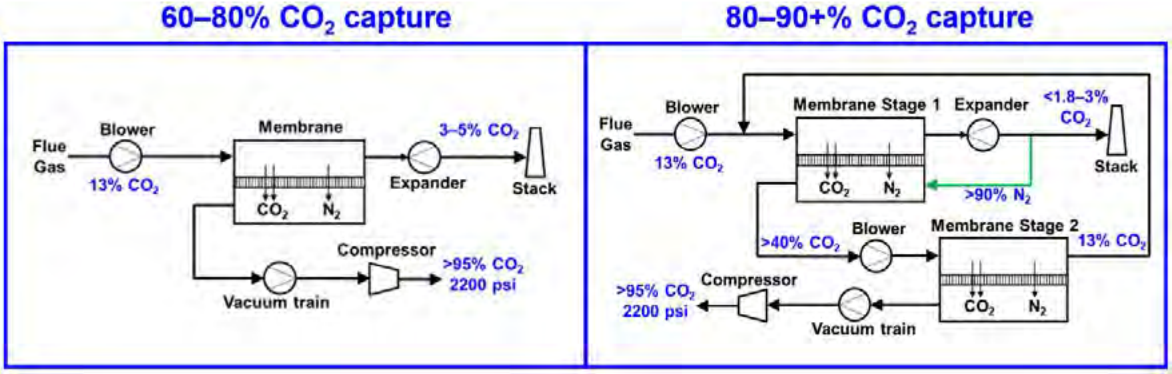

Figure 3: Flow diagrams of a one-stage membrane process to achieve 60–80% capture (left) and an innovative process to achieve >80% capture (right).

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	170	170
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	2,500	2,500
Manufacturing Cost for Membrane Material	$\$/m^2$	20	20
Membrane Performance			
Temperature	°C	77	77
CO_2 Pressure Normalized Flux	GPU or equivalent	3,500	3,500
CO_2/H_2O Selectivity	—	1	1
CO_2/N_2 Selectivity	—	160	160
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	spiral-wound, countercurrent	
Packing Density	m^2/m^3	ca. 2,000	
Permeate-Side Fluid	—	vacuum or retentate recycle	
Flue Gas Flowrate	ft^3/min	30.9	
CO_2 Recovery, Purity, and Pressure	%/%/bar	60–90 >95 1	
Pressure Drops Shell/Tube Side	psi/m	1.5/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	21.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.79 psia	135°F	12.46	14.97	68.12	3.64	0.81	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance – Resist up to 3 parts per million volume (ppmv) SO_2 and NO_2, respectively.

Flue Gas Pretreatment Requirements – Removal of particulates; SO_2 and NO_2 polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – Nitrogen with water, about 1% CO_2, and minor impurities.

Process Design Concept – Flowsheet diagrams shown in Figure 3.

Proposed Module Design – See Figure 1 (left).

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS (90% CAPTURE)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	40.3	40.0
Capital Expenditures	\$/MWhr	19.8	20.0
Operating Expenditures	\$/MWhr	10.5	12.0
Cost of Electricity	\$/MWhr	100.5	100.4

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS (70% CAPTURE)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	33.6	30.0
Capital Expenditures	\$/MWhr	10.6	10.5
Operating Expenditures	\$/MWhr	6.8	7.0
Cost of Electricity	\$/MWhr	85.9	86.0

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 4” report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*).

Scale of Validation of Technology Used in TEA – Bench-scale testing.

Qualifying Information or Assumptions – A direct contact cooler is not needed to condition the flue gas since the membrane is operated at 77°C. The purchased equipment cost for the turbo expander is $300/kWe based on literature data.

technology advantages

- Simplicity of membrane design leads to low-cost membranes.
- High CO_2 selectivity due to facilitated transport mechanism.
- Sensitivity study suggests that the COE at 70% CO_2 capture can be ca. 30% less than the DOE baseline approach.

R&D challenges

- Membrane stability in the presence of high-level contaminants, such as SO_2 and nitrogen oxide (NO_X).
- Corrosion or particulates fouling of membrane system equipment.

status

OSU has successfully developed their Gen II membrane, which has CO_2 permeance of 3,500 GPU and CO_2/N_2 selectivity of 160. Long-term stability was confirmed on simulated flue gas for the OSU Gen II membrane and on simulated and actual flue gas at the National Carbon Capture Center (NCCC) for the OSU Gen I membrane. The TEA based on bench-scale data suggests the membrane can achieve ca. 30% reduction in COE for a 70% CO_2 capture rate with a one-stage process compared with the DOE baseline approach and ca. $40/tonne for a 90% CO_2 capture rate with an innovative two-stage process. Current efforts are focusing upon designing an engineering-scale CO_2 capture system using OSU’s transformational membrane and process for field testing at ITC. Fabrication and testing of prototype membrane and commercial-sized membrane modules are currently underway.

available reports/technical papers/presentations

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, Howard Meyer, and John Marion, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” Project kickoff meeting presentation, Pittsburgh, PA, July 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11034&filename=Engineering+Scale+Design+and+Testing+of+Transformational+Membrane+Technology+for+CO2+Capture.pdf*.

Shiguang Li, Yang Han, Winston Ho, Travis Pyrzynski, Weiwei Xu, and Howard Meyer, “Engineering Scale Design and Testing of Transformational Membrane Technology for CO_2 Capture,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/S-Li%2C-GTI-Transformational-Membrane-Testing.pdf*

Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture

primary project goal

The University of Illinois at Urbana-Champaign (UIUC) advances the development of a novel biphasic carbon dioxide (CO_2) absorption process (BiCAP) and validates its technical advantages by testing an integrated system at a 40-kilowatt-electric (kWe) bench scale with actual coal-derived flue gas. The novel water-lean biphasic solvents have previously demonstrated (FE0026434) the desired vapor-liquid equilibrium (VLE) behavior, rapid absorption kinetics, and high stability in lab-scale characterization experiments, and individual major process steps have been tested on the lab-scale equipment or assessed by modeling studies. This project moves the technology development forward via fully integrated bench-scale testing in a relevant flue gas environment.

technical goals

- Develop process simulations using an Aspen Plus model to determine the optimal process configuration and operating conditions.
- Investigate biphasic solvent losses, emission control, and reclamation of the degradation products.
- Design, fabricate, and test a 40-kWe integrated bench-scale biphasic solvent-based capture unit with simulated flue gas. A subsequent test will use a flue gas slipstream from a coal-fired power plant.
- Assess the techno-economic performance of the technology integrated into a net 650-megawatt-electric (MWe) coal-fired power plant.
- Analyze technology gaps and potential environmental, health, and safety (EH&S) risks to advance the technology toward further scale-up and commercialization.

technical content

The BiCAP utilizes biphasic solvents, which are water-lean solvent blends, that can form and develop dual liquid phases, with the absorbed CO_2 highly enriched in one of the phases and lean solvent in the other. The phase transition behavior of a biphasic solvent is illustrated in Figure 1. The process features multiple stages of liquid-liquid phase separation (LLPS) during CO_2 absorption to maximize the CO_2 absorption kinetics and minimize the increase in solvent viscosity.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Biphasic Solvents for Post-Combustion CO_2 Absorption in Coal Flue Gas

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031600

predecessor project:

FE0026434

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partners:

Trimeric Corporation

start date:

4.06.2018

percent complete:

90%

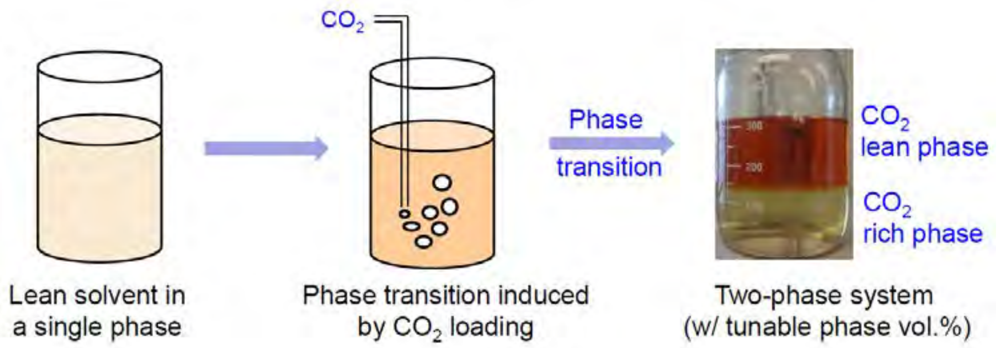

Figure 1: Phase transition behavior of a biphasic solvent.

A schematic diagram of the BiCAP is shown in Figure 2. The flue gas, after the cooling and sulfur dioxide (SO_2) polishing stages, enters the absorption column, which contains multiple stages of packed beds, and the CO_2 is absorbed into a biphasic solvent. At each stage, upon CO_2 loading, the biphasic solvent undergoes a phase transition and forms dual liquid phases. The heavy, CO_2-enriched phase is separated and pumped to a rich solvent tank. The CO_2-lean phase then flows via gravity to a heat exchanger to reduce the solvent temperature before entering the next stage of the packed bed. At the last stage, the solvent exiting the absorber is sent to an LLPS tank, in which the CO_2-enriched phase is pumped into the rich solvent tank. Both the hot and cold rich solvents are fed to a flash/stripper to remove CO_2, while the CO_2-lean phase is mixed with the regenerated solvent from the CO_2 stripper before recycling to the absorber. The CO_2 product streams from both the flash and stripper are cooled and compressed.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	60-240	<230
Normal Boiling Point	°C	140-300	>140
Normal Freezing Point	°C	-30 to 110	<20
Vapor Pressure @ 20 °C	bar	1×10^{-5} to 4×10^{-3}	$<1.0 \times 10^{-3}$
Manufacturing Cost for Solvent	$/kg	3-10	<15
Working Solution			
Concentration	kg/kg	0.6-0.8	>0.5
Specific Gravity (15 °C/15 °C)	-	~1.0	0.9–1.4
Specific Heat Capacity @ STP	kJ/kg-K	2.5–3.5	<3.5
Viscosity @ STP	cP	2-15	<20
Absorption			
Pressure*	bar	0.05 (equilibrium P_{CO2} at absorber bottom)	<0.07
Temperature	°C	40	30–50
Equilibrium CO_2 Loading	mol/mol	0.375-0.625 (0.7-1.0 in CO_2-enriched phase)	>0.375
Heat of Absorption	kJ/mol CO_2	65-85	~75
Solution Viscosity	cP	5–10/30–50 (upper/lower phases)	<50 (CO_2-enriched phase)
Desorption			
Flash			
Pressure**	bar	4-9 (5-11 in total)	≥7 (10 in total)
Temperature	°C	100-140	<140

Equilibrium CO_2 Loading	mol/mol	0.4-0.7	
Stripping (lean solution)			
Pressure***	bar	2-5 (3-7 in total)	≥3 (≥4 in total)
Temperature	°C	120-150	<150
Equilibrium CO_2 Loading	mol/mol	0.05-0.35	<0.35
Heat of Desorption (flash + stripping)	kJ/mol CO_2	65-85	~75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	not available	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >99% / >4	
Absorber Pressure Drop	Bar	0.14	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	not available	

*CO_2 partial pressure in the flue gas; **CO_2 partial pressure exiting flash; ***CO_2 partial pressure exiting stripper.

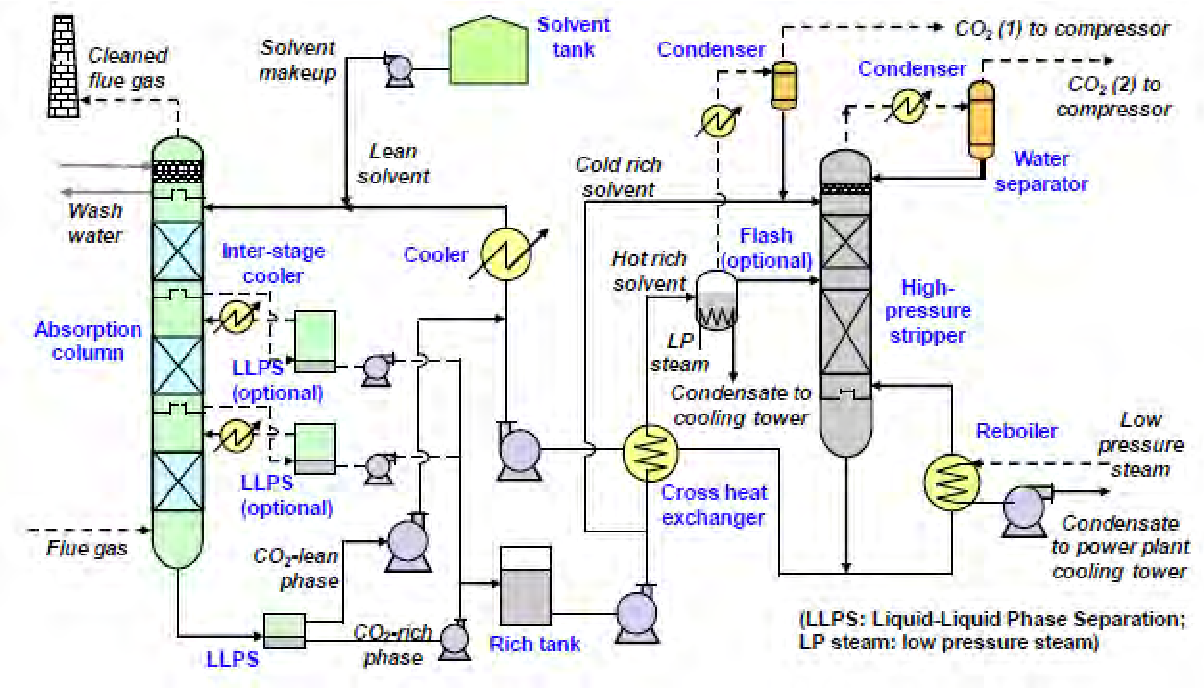

Figure 2: Schematic diagram of the BiCAP with multiple stages of LLPS.

Key features of the BiCAP include: (1) a unique process configuration of multi-stage CO_2 absorption and phase transition allows continual separation and removal of the CO_2-enriched liquid phase, maintaining rapid kinetics and low solvent viscosity throughout CO_2 absorption; (2) only the CO_2-enriched liquid phase is used for CO_2 desorption, thus lowering the mass flow of solvent required for regeneration; (3) a combination of flash and CO_2 stripping operations allows the high pressure of CO_2 desorption to further improve the energy efficiency; and (4) a portion of cold feed stream enters the stripping column, bypassing the cross heat exchanger, further reducing the stripping heat requirement.

In a previous U.S. Department of Energy (DOE)-funded project (FE0026434), the BiCAP was tested at laboratory scale (10 kWe) and exhibited a 34% reduction in parasitic power requirements and twice the CO_2 working capacity for desorption when compared with a process using the amine-based solvent, monoethanolamine (MEA). After determining the optimal process configuration and operating conditions, the team has designed and fabricated the 40-kWe integrated bench-scale capture unit. Parametric testing for two of the best-performing biphasic solvents identified from previous research (FE0026434) has been conducted with simulated flue gas at UIUC's Abbott power plant. One selected biphasic solvent is being further evaluated with a slipstream of coal-derived flue gas at the power plant. The team will use the test results to prepare a techno-economic analysis (TEA), as well as an analysis of the technology gaps and potential EH&S

risks, to advance the technology for further scale-up and commercialization. The system-wide results of this analysis are shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS*

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	40.4	30.0
Cost of Carbon Avoided	\$/tonne CO_2	50.7	37.7
Capital Expenditures	\$/MWhr	60.4	51.9
Operating Expenditures	\$/MWhr	56.1	55.5
Cost of Electricity	\$/MWhr	116.5	107.4

*Estimated based on DOE/NETL baseline Cases 11 and 12, Revision 2a, September 2013, DOE/NETL-2010/1397 and Updated Costs (June 2011 Basis), August 2012, DOE/NETL-341/082312.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The developed solvent belongs to a new class of biphasic solvents. The solvent is a blend of amines or the like and is a water-lean system containing less than 30 wt% water. The solvent absorbs CO_2 through chemical reactions between amines and CO_2. The solvent undergoes a phase transition to form dual liquid phases based on the difference of hydrophobicity between different species.

Solvent Contaminant Resistance – The developed biphasic solvent is highly resistant to oxygen and heat. Experiments revealed that the oxidative degradation of the biphasic solvent was eight times slower than the benchmark MEA under similar absorption conditions and its thermal stability at 150°C was comparable to the benchmark MEA at 120°C.

Solvent Foaming Tendency – No foaming issue was observed for the biphasic solvent, either in a gas bubbler tested continually for two weeks or in a laboratory absorption column operated intermittently for several months.

Flue Gas Pretreatment Requirements – The flue gas leaving the FGD needs be further polished to reduce the content of SO_2 below 10 parts per million volume (ppmv).

Solvent Makeup Requirements – Laboratory solvent stability experiments indicate that the makeup requirement of the biphasic solvent is lower than the benchmark MEA (i.e., less than 2 kg/ton CO_2 captured).

Waste Streams Generated – Waste streams from the BiCAP are similar to those from amine-based processes, including flue gas condensate, water wash blowdown, cooling water blowdown, heat stable salts, spent solvent wastes, and spent solvent reclamation materials (e.g., activated carbon).

Process Design Concept – See Figure 2.

technology advantages

- BiCAP maintains rapid kinetics throughout the CO_2 absorption process and thus can reduce the footprint and cost of absorption equipment compared with either MEA or other biphasic solvent-based processes.
- BiCAP can maintain the solvent at a lower viscosity and thus retain rapid mass transfer in the absorber, potentially increasing the CO_2 working capacity of the solvent and reducing the footprint and capital cost of the absorber.
- The combination of flash and stripping operations achieves high-pressure CO_2 desorption and thus lowers the energy use for CO_2 separation and compression.
- BiCAP desorption configuration with a cold rich solvent stream directly fed to the top of the stripper, in addition to the main rich solvent feed, results in reduced water vapor in the CO_2 stream and thus further reduces the stripping heat duty.
- The energy efficiency advantages of the BiCAP coupled with reduced equipment sizes when scaled-up for commercial systems leads to reductions in both capital and operating expenses compared to the benchmark MEA process.

R&D challenges

- Developing methods for controlling solvent losses caused by volatility of the selected biphasic solvents.
- Identifying the optimal process design and operating conditions for the proposed BiCAP.
- Developing methods for solvent reclamation with high efficiency and low environmental impact.
- Demonstrating reliable operation and stable performance of the bench-scale unit in an actual power plant environment.

status

Parametric testing for BiCAP1 and BiCAP2 biphasic solvents and the benchmark MEA using synthetic flue gas have been completed. Slipstream testing with real flue gas from the Abbott power plant started in late January 2022 and is currently underway.

available reports/technical papers/presentations

Lu, Y., 2021, “Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture.” Presented at the 2021 NETL/DOE Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lu.pdf*.

Nielsen, P. et al., 2021, "Modeling, Design, and Testing of a Novel Biphasic Solvent-Enabled Absorption System for Post-Combustion Carbon Capture," In the Proceedings of the 15th Greenhouse Gas Control Technologies Conference, Virtual. *https://papers.ssrn.com/sol3/papers.cfm?abstract_id=3812737.*

Lu, Y., 2019, “Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture,” 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/Y-Li-UIUC-Novel-Biphasic-Solvent.pdf*.

Nielsen, P., 2018, “Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture.” 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/P-Nielsen-UIUC-Biphasic-Solvent-Enabled-Absorption-Process.pdf*.

Lu, Y., 2018, “Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture.” kickoff meeting presentation. *https://netl.doe.gov/projects/plp-download.aspx?id=10472&filename=Development+and+Bench-Scale+Testing+of+a+Novel+Biphasic+Solvent-Enabled+Absorption+Process+for+Post-Combustion+Carbon+Capture.pdf*.

Du, Y. et al., 2018, “A Novel Water-Lean Biphasic Solvent System for CO_2 Capture,” presented at the 4th University of Texas Conference on Carbon Capture and Storage, Austin, TX.

Sachde, D. et al., 2018, “Economic Analysis of a Water-Lean Biphasic Solvent,” presented at the 4th University of Texas Conference on Carbon Capture and Storage, Austin, TX.

Du, Y. et al., 2017“A Novel Biphasic Solvent for Post-Combustion CO_2 Capture,” presented at the 4th Post-Combustion Capture Conference, Birmingham, AL.

Lu, Y., 2017, “Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture,” presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA.

Lu, H. et al., 2017, “Bench-Scale Testing of CO_2 Absorption with a Biphasic Solvent in an Absorption Column with Staged Phase Separations,” presented at the 2017 Carbon Capture, Utilization & Storage Conference, Chicago, IL.

Lu, Y., 2017, “Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture,” Budget Period 1 Project Review Meeting presentation, Pittsburgh, PA.

Lu, Y., 2016, “Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/Y-Lu-ISGS-Biphasic-CO2-Absorption-Process.pdf*.

Ye, Q. et al., 2015, “Screening and Evaluation of Novel Biphasic Solvents for Energy-Efficient Post-Combustion CO_2 Capture,” International Journal of Greenhouse Gas Control, Volume 39, pp. 205-214.

ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds

primary project goal

Gas Technology Institute (GTI), with Clean Carbon Solutions Ltd. (CCSL), are developing and validating a transformational carbon dioxide (CO_2) capture technology (ROTA-CAP) using novel rotating packed-bed (RPB) absorbers and regenerators combined with an advanced solvent toward providing an economically viable carbon capture system.

technical goals

- Design, construct, and commission the ROTA-CAP equipment at GTI.
- Develop a preliminary process model and perform an initial fabrication feasibility study for commercial process.
- Test the ROTA-CAP system with simulated flue gases and natural gas burner flue gas at GTI to determine key operating parameters.
- Calibrate the process model and measure solvent carryover.
- Perform long-term reliability and operability testing at the National Carbon Capture Center (NCCC) on coal-fired flue gas.
- Verify the process model.
- Determine scale-up challenges, solvent degradation, and aerosol formation.
- Complete a high-level techno-economic analysis (TEA).

technical content

The RPB contactor design comprises a rotating disk of packing material that generates a high gravity centrifugal force, which distributes solvent radially toward the outer edge of the disk, providing a high surface area for mass transfer to occur as countercurrent flue gas contacts the solvent droplets. An integrated absorber-regenerator bench-scale test skid for the ROTA-CAP system is being designed, constructed, and operated at GTI using simulated flue gas and natural gas burner flue gas to determine key operating parameters. See Figure 1 for a schematic of RPBs in gas-liquid contactor operation. CCSL is providing an advanced solvent for the test, such as its proprietary amine-promoted buffer salt (APBS) solvent. To compare the performance of ROTA-CAP to the conventional process using commercial monoethanolamine (MEA) solvent, the team is utilizing the Slip Stream Test Unit (SSTU) at NCCC. See Figure 2 for a general bench-scale ROTA-CAP skid process flow diagram. Long-term (1,000-hour) stability testing of the integrated ROTA-CAP CO_2 capture system will be conducted on a coal-fired flue gas slipstream at NCCC at a scale of 1 tonne CO_2 per day, and the collected data will be used to determine solvent degradation and aerosol formation. A simulation process model is being developed for integrated RPB carbon capture systems and will be used to aid in larger-scale deployment of the ROTA-CAP technology, such as integration with coal-fired power plants. A high-level TEA of the process will be performed based on experimental data and the capture process model verified with the long-term operation data.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Rotating Packed Bed with Advanced Solvent

participant:

Gas Technology Institute

project number:

FE0031630

predecessor projects:

N/A

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partners:

Clean Carbon Solutions Ltd.; National Carbon Capture Center

start date:

10.01.2018

percent complete:

90%

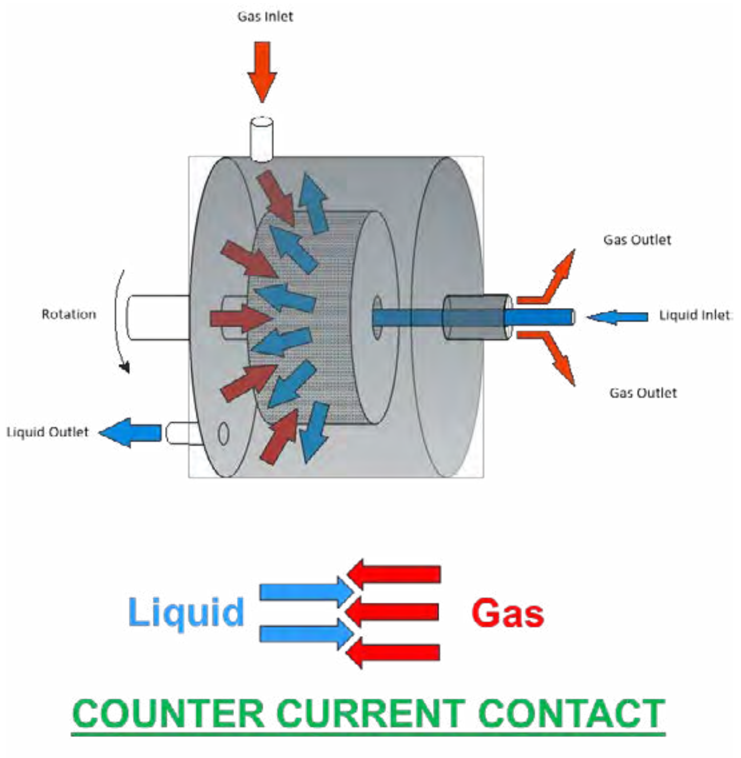

Figure 1: RPB gas-liquid contactor.

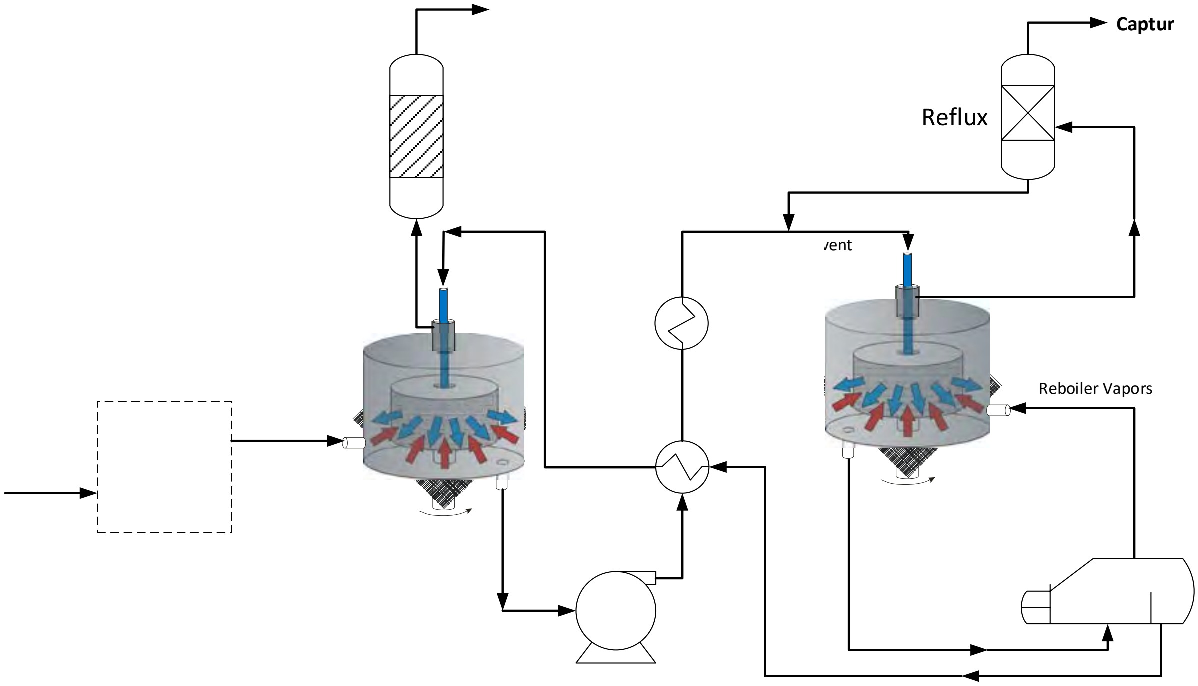

Figure 2: ROTA-CAP bench-scale test skid process flow diagram.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	57.29	57.29
Normal Boiling Point	°C	104-220	104-220
Normal Freezing Point	°C	N/A	N/A
Vapor Pressure @ 15°C	bar	18.2	18.2
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.425	0.425-0.55
Specific Gravity (15°C/15°C)	—	1.007	>1.007
Specific Heat Capacity @ STP	kJ/kg-K	3.344	>3.344
Viscosity @ STP	cP	2.839	>2.839
Absorption			
Pressure	bar	0.1	0.1
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	3.3	>3.3
Heat of Absorption	kJ/mol CO_2	75.2	>75.2
Solution Viscosity	cP	4.4	>4.4
Desorption			
Pressure	bar	0.07	0.07
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.7	>0.7
Heat of Desorption	kJ/mol CO_2	2.7-3.0	2.55-2.85

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The solvent utilizes a chemical reaction with acid gases to remove them from the feed gas stream. The reaction is reversed in the stripper unit operation through the application of heat to the solvent.

Solvent Contaminant Resistance – Besides physical contamination (e.g., feed gas solids), the main contaminant expected in the solvent is heat-stable salts (HSSs). HSSs are a byproduct of heat and solvent reaction with components in the feed gas (e.g., oxygen [O_2], nitrogen oxide [NO_X], sulfur oxide [SO_X]). In long-term testing by CCSL, the solvent has superior resistance to HSS generation when compared to other commercial solvents.

Solvent Foaming Tendency – Foaming has not been reported in any test campaign or commercial operation of the solvent to date.

Flue Gas Pretreatment Requirements – Pretreatment would include:

- Reduction of particulate matter, NO_X, and SO_X to current U.S. Environmental Protection Agency (EPA) limits.
- Cooling and water saturation of the feed gas to approximately 110°F.

Solvent Makeup Requirements – Solvent makeup is minimal as HSS generation and physical loses should be low. It is expected that less than 0.35 kg solvent per tonne of CO_2 should be added intermittently.

Waste Streams Generated – A water bleed is expected from the regenerator reflux to maintain the solvent concentration and remove any trapped ammonia salt species. During long-term testing, HSSs could be removed through reclaiming. The HSS sludge would need to be disposed. However, with only a 1,000-hour target for the long-term testing, reclaiming is not anticipated during this test campaign.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	68	30
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/ tonne CO_2	42	12
Operating Expenditures	\$/ tonne CO_2	26	18
Cost of Electricity	\$/MWhr	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The current research and development (R&D) value is based on a pre-front-end engineering design study conducted by CCSL with an independent engineering, procurement, and construction firm. The study evaluated capital costs for a 100 tonne per day (TPD) RPB system. The operating expenses are based on using CCSL commercial solvent. The target R&D values are for a projected 500 TPD RPB system. Savings in RPB manufacturing, packing fabrication, plot plan reduction, and utilizing an intensified solvent are included.

All costs are for the carbon capture island only. The typical unit operations include a booster fan, direct contact cooler, absorber, regenerator, pumps, and heat exchange.

Carbon dioxide product handling and transportation, site preparation, and duct connections are excluded.

The cost of capture economics, reported as 2021 USD, are based on:

- 25-year project lifetime.
- 8% discount rate.
- 3% escalation over the life of the project.
- 350-days-per-year operation.
- $3.50/MMBtu heat source.
- $0.05/kWh electricity.
- $2/1,000 gallons cooling water make-up.
- $39/gallon solvent.

technology advantages

- The RPB technology provides intense micromixing and internal mass transfer, thereby facilitating significant size reductions in the absorber and regenerator relative to conventional columns, resulting in lower capital costs.
- The use of a highly concentrated solvent, such as CCSL's APBS solvent, reduces the regeneration energy and leads to greater process efficiency.
- Reduced oxidative and thermal degradation.
- Decreased solvent top-up requirements by approximately 77%.
- Reduced waste handling and disposal cost by up to 92%.
- A simulation process model for integrated RPB carbon capture systems will be developed, which can be used in future larger-scale deployments.
- TEA will evaluate the value of the ROTA-CAP technology in the carbon capture market.
- RPB reactors are non-selective to the solvent used.
- RPB reactors offer higher efficiencies.

R&D challenges

- The integrated use of RPBs as both absorber and regenerator in a single system.
- The mechanical design parameters of rotating equipment.
- Solvent stability performance during operation.
- Integrating and achieving required solvent regeneration using an RPB regenerator.
- During testing, GTI will determine the solvent performance and modify it as needed to achieve a 90% CO_2 removal rate. The optimum CO_2 removal rate to achieve the lowest cost of removal will be calculated.
- Scale-up limitations exist with rotating equipment. Modular design may be useful to overcome size limitations of RPBs for larger systems. Capital cost and added complexity of the system will need to be managed.

status

GTI designed and costed the bench-scale ROTA-CAP test skid, a 50-kilowatt-electric (kWe) (1,000-kg/day CO_2 removal) equivalent-scale integrated carbon capture skid. The skid has a flue gas cooling and filtration section available to be used when necessary.

The key variables tested include:

- RPB rotational speed of 100 to 600 RPM.

- Absorber liquid/gas ratio of 0.5 to 5.0 kg/m^3.
- Solvent circulation rate of 30 to 150 kg/h.
- Solvent concentration/viscosity of 35 to 70 wt% (5–80 cP).
- Regenerator operating pressure/temperature of 0.0–1.0 bar(g) (100–130°C).
- Flue gas composition (synthetic, natural gas-fired, coal-fired).

Test skid construction and testing with synthetic gas and natural gas-fired flue gas with elevated CO_2 concentration (10.4% vol.) was completed by the fourth quarter of 2021. The task duration for testing of the bench-scale ROTA-CAP skid at GTI was about five months. After this test period the skid was transported to and operated at NCCC with natural gas-fired flue gas containing 10.4% CO_2. The test skid is currently at NCCC and testing will resume after NCCC shutdown to complete the long-term 1,000-hour testing in 2022.

available reports/technical papers/presentations

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," August 2021 Carbon Management and Oil and Gas Research Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Akpolat.pdf*.

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," Budget Period 1 Review Meeting, Pittsburgh, PA, March 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10540&filename=ROTA-CAP+-+An+Intensified+Carbon+Capture+System+Using+Rotating+Packed+Beds.pdf*.

Akpolat, O., H. Meyer, D. Bahr, "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/O-Akpolat-GTI-ROTA-CAP.pdf*.

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/O-Akpolat-GTI-Rotating-Packed-Beds.pdf*.

Akpolat, O., H. Meyer, W. Shimer, D. Bahr, J. Hall, "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," Project Kickoff Meeting, Pittsburgh, PA, Dec 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10538&filename=ROTA-CAP+-+An+Intensified+Carbon+Capture+System+Using+Rotating+Packed+Beds.pdf*.

Emissions Mitigation Technology for Advanced Water-Lean Solvent-Based CO_2 Capture Processes

primary project goal

Research Triangle Institute (RTI) is developing a comprehensive solvent emission mitigation toolset for reducing the solvent and aerosol emissions from carbon dioxide (CO_2) capture systems using water-lean solvents (WLSs). Due to their low energy requirement for solvent regeneration, lower regeneration temperature, low corrosivity, and low vapor pressure, WLS systems are rapidly being developed for CO_2 capture. RTI's toolset is specifically designed for WLS systems, implementing an advanced organic solvent wash system in conjunction with water wash, acid wash, and other commercially available, state-of-the-art emission reduction technologies.

technical goals

- Characterize and understand the emissions produced by WLSs while capturing CO_2.
- Develop an empirically derived emissions model based on the solvent physical properties and on critical operating parameters from the absorber and wash section.
- Evaluate suitable process arrangement for emission-reduction devices.
- Demonstrate the effectiveness of these emission mitigation devices on the bench-scale CO_2 capture system optimized for WLSs.

technical content

RTI is advancing development of an effective toolset to reduce amine emissions for WLSs by means of reducing the vapor loss, liquid entrainment, and aerosol formation altogether. The project team will characterize the emissions produced by WLSs while capturing CO_2; develop a model that predicts the emissions based on the solvent's physical and chemical properties on critical operating parameters from the absorber and wash section; develop a process toolset for emissions reduction over a range of solvent systems; evaluate the effectiveness of these emissions mitigation devices in a bench-scale (6-kilowatt [kW]) CO_2 capture system by testing with RTI's current WLS formulation, NAS-5 (non-aqueous solvent-5), and a second selected WLS under actual flue gas conditions; and complete a techno-economic analysis (TEA) to determine the contribution of the emissions control technologies (ECTs) to the overall CO_2 capture cost.

The results obtained in this study will assist in process scalability, mitigate the technology's risk associated with emissions, improve the economic potential, and aid in the commercial adoption of WLSs.

The project tasks will determine RTI's NAS and selected WLS emissions characteristics from the absorber column; develop an empirical emissions model

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Water-Lean Solvent Emission Control

participant:

Research Triangle Institute

project number:

FE0031660

predecessor projects:

N/A

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partners:

Technology Centre Mongstad; Linde

start date:

10.01.2018

percent complete:

93%

based on critical operating parameters; screen organic solvents and amine adsorbents; and determine, implement, and evaluate the effectiveness of the ECTs at RTI's Bench-Scale Gas Absorption System (BsGAS). Figure 1 shows the potential ECTs for WLS systems to be incorporated at a CO_2 capture plant. Also, the team will carry out the modifications based on RTI's findings and evaluate the amine emissions using NAS-5 and a selected WLS and refine the empirical emissions model/determine the impact of the ECTs to the CO_2 capture cost.

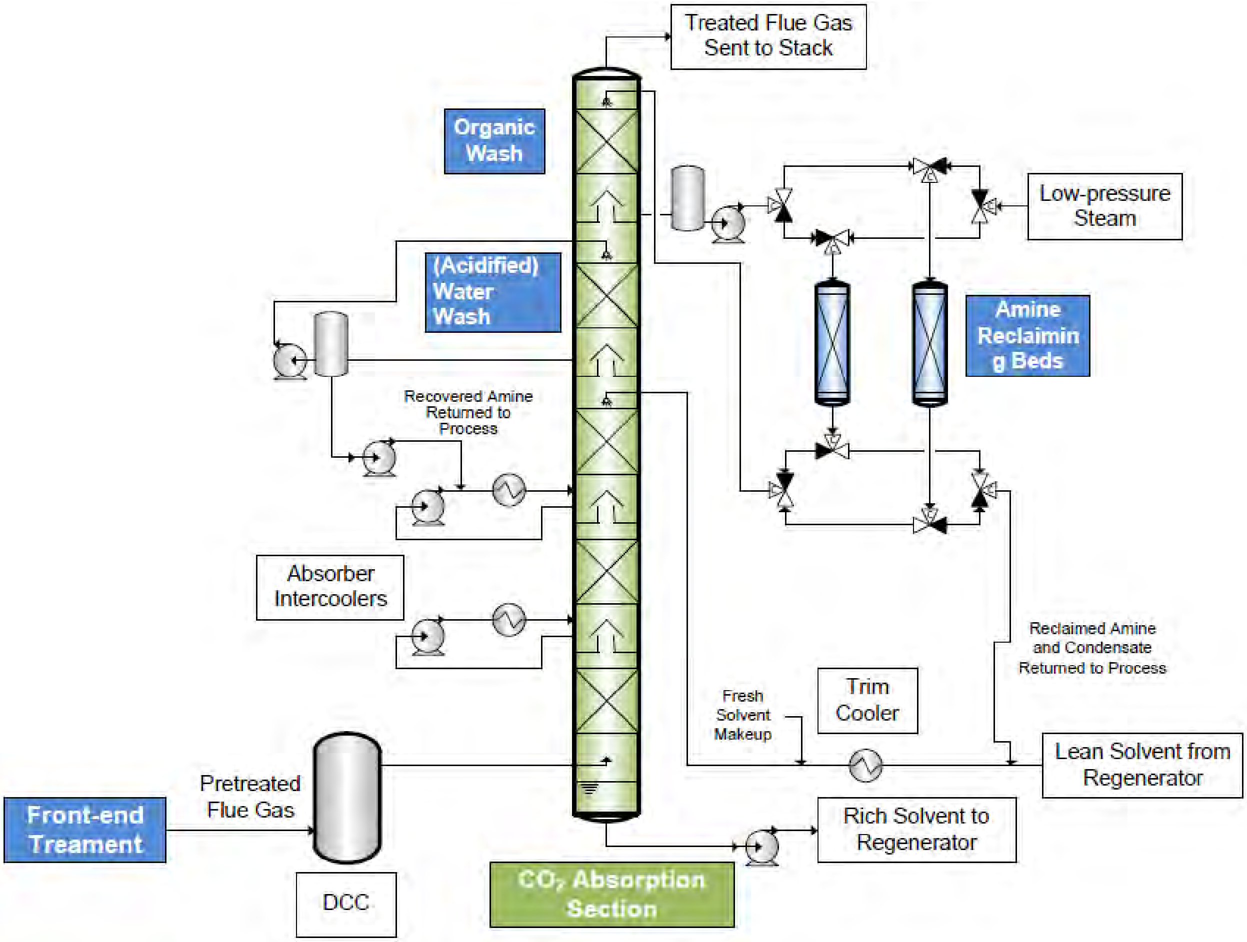

Figure 1: Potential ECTs for WLS systems to be incorporated at a CO_2 capture plant.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	$/kg	14	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38

Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/mol CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28
Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45-1.13*	0.45
Heat of Desorption	kJ/mol CO_2	2,100*	2,045
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

* Experimentally measured data.

** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxide (SO_X) and nitrogen oxide (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2 to 0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – Absorber with interstage coolers coupling with regenerator with interstage heaters.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS*

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	\$48.3	—
Cost of Carbon Avoided	\$/tonne CO_2	62.1	—
Capital Expenditures	\$/MWhr	457	—
Operating Expenditures	\$/MWhr	56	—
Cost of Electricity	\$/MWhr	\$124.67	—

*Economics parameters were not set as an R&D Target.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The calculation basis are the Case 11 for the reference plant and Case 12 for the CO_2 capture plant, provided by NETL for TEA analysis found in “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Revision 2a, September 2013” and the costs updated using “Updated Costs June 2011 Basis for Selected Bituminous Cases,” DOE/NETL-341/082312.

Scale of Validation of Technology Used in TEA – The TEA was performed using a process model validated with data from pilot and bench scale. The technology for CO_2 capture has been validated at the pilot plant scale. The technology for emissions control has been validated at bench-scale testing.

Qualifying Information or Assumptions – All numbers are provided using June 2011 cost basis. Capital expenditure costs were calculated using the total overnight cost (TOC).

technology advantages

- WLS system has a low energy requirement for solvent regeneration and other added benefits, which reduce cost of CO_2 capture.
- Project will provide a model that predicts the amine emissions using the solvent properties, key process parameters, and the recommended emissions mitigation devices required for solvents specific to the developers.

R&D challenges

- Aerosol particle generation.
- Development of aerosols and particle counts technique for WLSs.
- Quantification and speciation of the emissions from WLSs.
- Emissions model development.
- Solvent screening for organic wash section.
- Process arrangement for amine extraction.
- Parametric and long-term testing.
- TEA.

status

More than 2,000 hours of testing were completed for the BsGAS operation in the investigation of aerosols and ECTs. Various components of the prototype emissions control system were constructed for testing the use of WLSs for CO_2 capture. Solvent degradation testing systems were constructed to determine the oxidative degradation and chemical pathways for the formation of nitrosamines (NA) and amine component thermal degradation products. Various solid adsorbents were tested for their amine absorption capacity and ability to regenerate to identify potential sorbent candidates to be used for the amine BsGAS recovery unit.

RTI's NAS-5 was tested to evaluate the impact of various process parameters that affect the overall amine emissions and aerosols formation using BsGAS. The key parameters that were evaluated, and that could impact the emissions, were water wash temperature, liquid-to-gas ratio, CO_2 capture rate, and the temperature in the absorber. Additional water wash, advanced demister, CO_2 acidification tanks, and particulate filters were added to BsGAS in late 2019. The effectiveness of these devices in controlling the amine emissions were evaluated (Figure 2).

Various emissions reduction strategies for advanced WLSs were studied, including minimizing aerosols through optimizing NAS running condition and the addition of ECTs; minimizing degradation through antioxidant, thermal, and NO_X reduction studies; and minimizing vapor pressure through solvent formulation. The BsGAS with ECTs showed less than 10 parts per million (ppm) amine emissions when tested under simulated flue gas with aerosols.

RTI has developed a Principal Component Analysis (PCA) framework for an empirical model to predict aerosol-based emissions utilizing BsGAS. This model correlates the process parameters of a WLS CO_2 capture system that is based on BsGAS testing of a WLS.

The last phase of the project will include the installation and commissioning of the flue gas generation system, which aims to achieve less than 1 ppm emissions. Once the system is tested, the emission model and TEA will be updated.

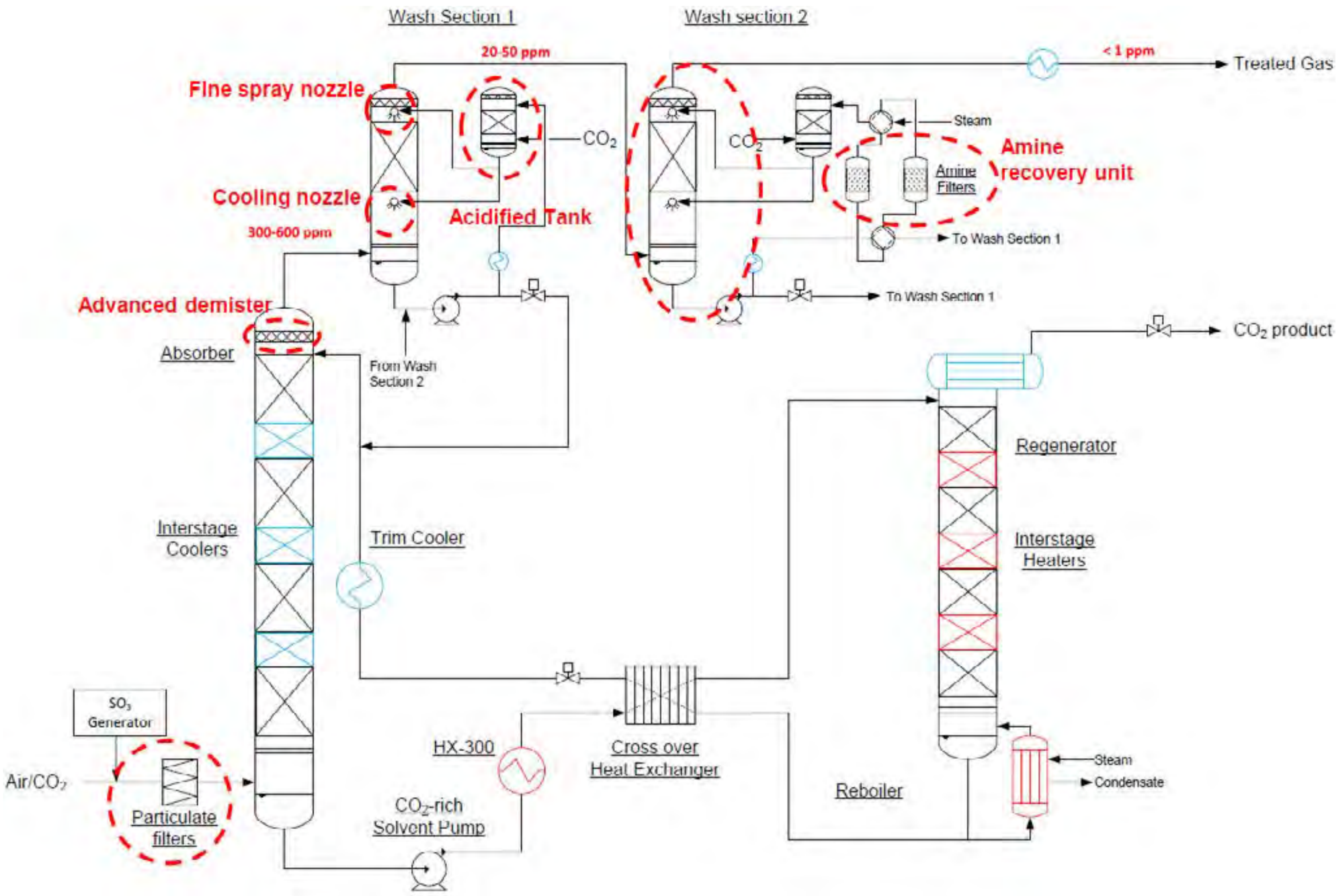

Figure 2: RTI's BsGAS with ECT and flue gas generation system.

available reports/technical papers/presentations

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Project kick-off meeting presentation, Nov 2018. *https://www.netl.doe.gov/sites/default/files/2019-01/FE0031660-kickoff.pdf.*

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Poster presentation by Jak Tanthana, RTI International, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://netl.doe.gov/sites/default/files/netl-file/J-Tanthana-RTI-Solvent-Emissions-Mitigation.pdf.*

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Tanthana-RTI-Solvent-Emissions-Mitigtion.pdf*.

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2020 Project Continuation Meeting, March 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10603&filename=Emissions+Mitigation+Technology+for+Advanced+Water-Lean+Solvent+Based+CO2+Capture+Processes.pdf.*

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2021 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Tanthana.pdf*.

Fog- and Froth-Based Post-Combustion CO_2 Capture in Fossil Fuel Power Plants

primary project goal

The University of Kentucky Center for Applied Energy Research (UKy-CAER) is developing a transformational compact carbon dioxide (CO_2) absorber with internal fog and froth formation, for use in a solvent-based post-combustion CO_2 capture process, to surmount the limitations of packed-bed CO_2 absorption columns and to lower the capital cost of carbon capture.

technical goals

- Design and fabricate a compact absorber with internal fog and froth sections.
- Develop and finalize the atomizing nozzle and froth-generating screens and operation conditions for fog and froth formation and destruction.
- Evaluate the fog and froth sections performance in a cold test unit.
- Complete a bench-scale parametric testing campaign followed by a long-term campaign to assess performance and investigate the effects of solvent degradation on fog and froth formation.
- Prepare a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

UKy-CAER is developing an open-tower compact absorber with internal fog and froth for enhanced solvent-based CO_2 capture, as shown in Figure 1. In the process, the flue gas enters the bottom of the absorber and contacts the solvent in a counter-current flow through a section containing structured packing, capturing approximately 30% of the total CO_2 before passing through a riser to the top of the fog/froth capture section. In this section, the gas first contacts a lean amine mist in a co-current flow in a temperature-controlled environment, with up to five times the liquid/gas contact area. Both the gas and liquid exiting from the fog section are forced through froth-generating and -propagating screens in the froth section. Here, also a temperature-controlled environment, the mass transfer is increased because a thin (target of ~10 µm) liquid film virtually eliminates the CO_2-amine diffusion resistance that typically impedes mass transfer in the conventional capture technologies. By greatly increasing the liquid/gas contact area and minimizing the diffusion resistance, the absorber column size can be reduced by up to 70% compared to a standard absorber design. Combining this fog/froth process with other UKy-CAER CO_2 capture technologies could potentially reduce the CO_2 capture capital cost by 57%.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

High Contact Compact Absorber

participant:

University of Kentucky Center for Applied Energy Research

project number:

FE0031733

predecessor projects:

N/A

NETL project manager:

Carl Laird
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partners:

Industrial Climate Solutions Inc.; NexantECA; ALL4

start date:

05.01.2019

percent complete:

77%

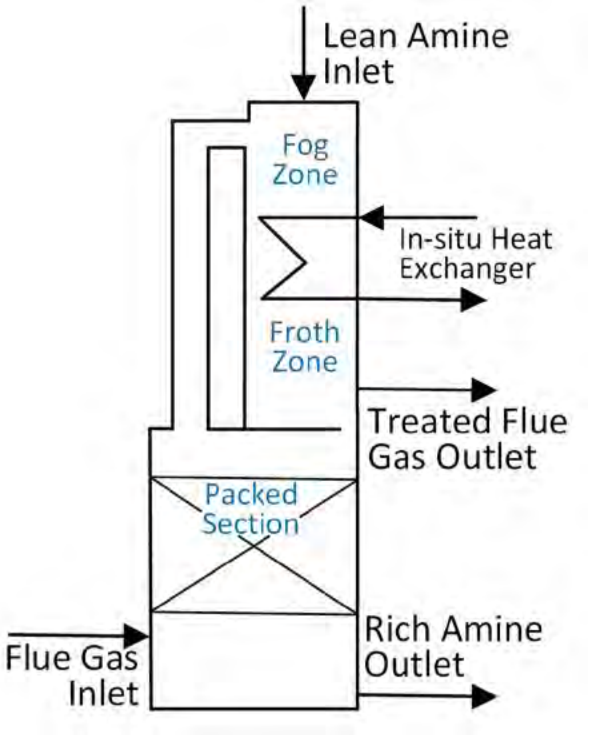

Figure 1: Schematic of University of Kentucky’s compact absorber.

The project is designing and fabricating the complete compact absorber, including the atomizing nozzle, froth-generating and -propagating screens, and in situ heat removal. The frothing screens, as shown in Figure 2, are optimized for froth generation and propagation. They are designed and supplied by Industrial Climate Solutions. Fog generation includes spray nozzle selection and optimization of the nozzle arrangement, as well as mist size distribution in the column, via liquid supply parameters and solvent properties. Individual testing of the fog section and froth section will be followed by parametric and long-term testing of the compact absorber integrated in UKy-CAER bench-scale post-combustion capture facilities using simulated and actual flue gas. Data from testing supports development of a TEA and EH&S assessment for the process.

Figure 2: Froth-generating and -propagating screens.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g/mol	Amine	Amine
Normal Boiling Point	°C	155-170	155-170
Normal Freezing Point	°C	-2	-2
Vapor Pressure @ 20°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg (pure chemical, small batch)	14.74	14.74
Working Solution			
Concentration	kg/kg	0.35 to 0.45	0.35 to 0.45
Specific Gravity (15°C/15°C)	-	~1.0	~1.0
Specific Heat Capacity @ 40°C	kJ/kg-K	2.7-3.3	2.7-3.3
Viscosity @ STP	cP	5-7	5-7
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5	0.45
Heat of Absorption	kJ/mol CO_2	~-65	~-70
Solution Viscosity	cP	3-5	3-5
Desorption			
Pressure	bara	3-5	3-5
Temperature	°C	110-130	110-130
Equilibrium CO_2 Loading	mol/mol	0.20	0.20
Heat of Desorption	kJ/mol CO_2	~85	~85
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	24	
CO_2 Recovery, Purity, and Pressure	% / % / bara	90 >95% 1.65	
Absorber Pressure Drop	bar	<20"WC	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$	$36K	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_X**	**NO_X**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, **T**, and carbon loading, **C/N**, can be expressed as: $\mathbf{R(T, C/N) = k_G \cdot a \cdot (P_{CO2} - P^*_{CO2})}$ where $\mathbf{k_G}$ is mass transfer coefficient, **a** is effective wetted surface area, and $\mathbf{(P_{CO2} - P^*_{CO2})}$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via $\mathbf{k_G}$ and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the aqueous system compared to any 2nd-generation technology because there is an order of magnitude greater effective wetted surface area in the top of the absorber.

Solvent Contaminant Resistance – UKy-CAER analysis show the solvent is more resistant to degradation, 40–50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – Unstable froth formation (not persistent foaming) is a key aspect to the compact absorber. Surfactant is added to reduce the surface tension and therefore control the frothing behavior. Initial CO_2 capture experiments on solvent physical properties were performed in a packed column (2-inch internal diameter [ID] mini-scrubber). Adding surfactant to change the solvent surface tension led to a CO_2 capture efficiency increase of 15–20% throughout the carbon loading range. The key reason for this enhancement is the presence of fine froth (bubbles) that increase surface area with the addition of surfactant. It was also found that as carbon loading increases, the tendency to form bubbles decreases due to increased viscosity and surface tension. For an unstable froth, the dispersion rate is also important. A surfactant was chosen with the faster dispersion rate compared to others considered.

Flue Gas Pretreatment Requirements – The flue gas pretreatment requirement is sulfur dioxide (SO_2) removal to less than 5 parts per million (ppm) to minimize heat stable salt formation. This can be done with a standard counter-current pretreatment column with a circulating solution of either of soda ash (Na_2CO_3) or sodium hydroxide (NaOH). The solvent used is a hindered primary amine and does not form stable nitrosamine species, therefore no additional nitrogen oxide (NO_X) removal is required. No additional moisture removal required, as it is for ionic liquids.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UKy-CAER analysis show the solvent has degradation rates less than 30 wt% MEA and when the UKy-CAER developed solvent recovery technology is applied, the solvent emission will be about 0.5 ppm. The anticipated solvent makeup rate is less than 0.5 kg/tonne CO_2 captured.

Waste Streams Generated – The waste streams of the post-combustion CO_2 capture process using the compact absorber are the same as any other post-combustion CO_2 capture process. There will be a blowdown stream from the SO_2 pretreatment column and a reclaimer waste stream from the solvent loop.

Process Design Concept – The design concept is shown in Figure 3. A 3-inch column is used for the fogging and frothing section where the flue gas and solvent flow in a co-current fashion. The bottom section contains typical structured packing with the flue gas and solvent moving in a counter-current fashion.

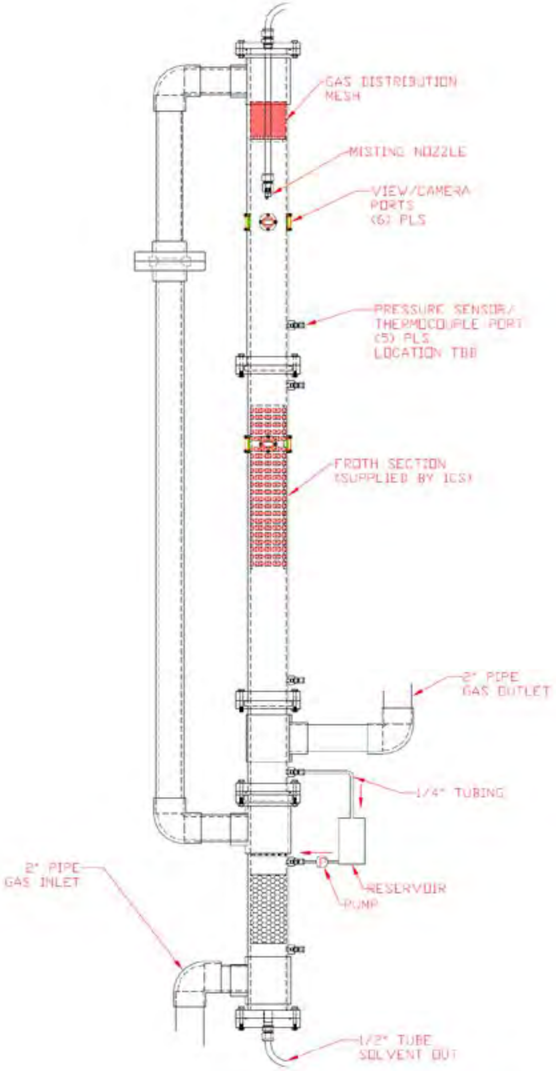

Figure 3: Compact absorber design concept.

Proposed Module Design – The absorber is modular with a natural divide between the bottom packed section and the top fog and froth section.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured (excluding TS&M)	2011$/tonne CO_2	31.95	—
Cost of Carbon Avoided (excluding TS&M)	2011$/tonne CO_2	37.00	—
Capital Expenditures	2011$/MWhr	52.98	—
Operating Expenditures	2011$/MWhr	11.36	—
Cost of Electricity (excluding TS&M)	2011$/MWhr	106.17	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in the table are based on the reference plant provided by the National Energy Technology Laboratory (NETL) for TEA, found in the “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity” report Revision 2a, $2011.

Scale of Validation of Technology Used in TEA – 0.1 megawatt-thermal (MWth) bench.

technology advantages

- Up to five times increase in liquid/gas contact area over structured packing.
- Up to four times increase in mass transfer over conventional columns due to a thin (target of ~10 µm) liquid film, eliminating the CO_2-amine diffusion resistance that can impede the overall mass transfer of a capture technology.
- Up to 70% reduction in absorber height.
- Up to 50% reduced pump power requirement.
- Maintain carbon loading as close as achieved with conventional column containing structured packing.
- Potential, when combined with other University of Kentucky CO_2 capture features, for a 57% reduction in capital cost for carbon capture.

R&D challenges

- Demonstration at the bench scale due to wall effects in the small column.
- Controlling the froth size.

status

The University of Kentucky has compared and selected options for the atomizing nozzle and frothing screens for their system. Fogging and frothing sections were designed, constructed, and connected with the existing 0.1-MWth facility. Both batch and continuous operations were conducted. The parametric campaign was completed after 827 hours of testing with bottled gas. More than 60% CO_2 capture and 0.45 mol C/mol N rich loading was demonstrated with a 3-foot fog and froth and 2-foot structured packing. This is on par with traditional absorber performance having greater than twice the amount of structured packing. The long-term campaign was conducted with approximately 1,000 hours of testing with fossil fuel-derived flue gas. The State Point Data Table was completed for the UKy-CAER hindered amine blend solvent. Work on the TEA is underway. The EH&S assessment will be conducted.

available reports/technical papers/presentations

Nikolic, H. “Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants,” Presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Nikolic.pdf*.

Nikolic, H. “Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants,” Presented at the CO_2 Capture BP1 Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=10750&filename=Fog+and+Froth+Based+Post+Combustion+CO2+Capture+in+Fossil+Fuel+Power+Plants.pptx*.

Nikolic, H. “Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKY-CAER-Fog-Froth-Capture.pdf*.

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High-Efficiency Post-Combustion Carbon Capture System

primary project goal

Precision Combustion Inc. (PCI), along with its partners University of Florida and the Commonwealth Scientific and Industrial Research Organization (CSIRO) Australia, is developing a compact, modular system utilizing high-capacity metal organic framework (MOF) nanosorbents in a unique low-pressure drop system design to capture carbon dioxide (CO_2) from flue gas. The combination of improved sorbent geometry with a cutting-edge nanomaterial with unsurpassed properties for CO_2 removal that can be produced at large scale allows for a high-efficiency CO_2 capture unit that can be easily retrofitted to existing power plants.

technical goals

- Optimize the sorbent to higher capacities with good selectivity toward CO_2, as well as resistance to humidity and contaminants.
- Optimize mesh geometry and coating process to achieve higher loadings without affecting sorbent structure at increased production capacity.
- Simulate a scaled-up plant design with steady and dynamic process and CFD modeling of the system.
- Assemble small-scale module and test with actual coal-derived flue gas to show the efficacy of the system and further refine the operating conditions.
- Integrate with DOE's CCSI software.
- Perform full-scale techno-economic modelling of CO_2 capture with sensitivity analysis.

technical content

PCI is developing a post-combustion carbon capture system using high-capacity MOF nanosorbents coated on PCI's patented Microlith® mesh sorbent substrate.

MOF materials are crystalline organic-inorganic compounds formed by coordination of metal clusters or ions with organic linkers—usually bivalent or trivalent aromatic carboxylic acids or nitrogen-containing aromatics. They have extremely high surface area, high pore volume, uniform size pores, and high metal content, making them excellent candidates for selective CO_2 capture. The MOF materials retain CO_2 at up to six times the capacity of amine solutions under low pressure and high humidity conditions, and also require significantly less energy for regeneration and exhibit a lower rate of degradation due to the capture of CO_2 via physical adsorption rather than through chemical reaction. The modular cartridge form factor enables low-cost retrofit to existing systems. To achieve high space velocity sorption, the densified nanostructured sorbent is coated on PCI's patented mesh-based substrate, trademarked Microlith, that has higher surface area per unit volume and much higher mass transfer coefficients compared to other substrates. The the improved sorbent geometry enables decreased bed volume with equivalent effectiveness to other types of monolithic or loose packing, without pressure drop penalty. Additionally, up to 20 times higher mass and heat transfer coefficients are obtainable as compared to other sorbent systems, such

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Metal Organic Framework Nanosorbent on Microlith Substrate

participant:
Precision Combustion Inc.

project number:
SC0017221

predecessor projects:
N/A

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partners:
University of Florida;
Commonwealth Scientific and Industrial Research Organization (CSIRO) Australia

start date:
02.21.2017

percent complete:
97%

as monoliths and pellets, due primarily to boundary layer minimization and break-up, boosting CO_2 removal rates with greater sorbent bed utilization and less bypass inherent to packed beds or monoliths. This sorbent manufacturing technology allows for adherent and durable MOF coatings (as well as alternative future high surface area sorbents) on the Microlith substrate. Sorbent coated on Microlith mesh is shown in Figure 1.

The process as shown in Figure 2 includes a modular capture system containing the MOF nanosorbents coated on Microlith, with adsorption at 30°C and desorption at 80°C. This capture system configuration enables low-pressure drop, high volumetric utilization, and high mass transfer, and also has a low energy of regeneration.

In Phase I, a proof-of-concept of the Microlith substrate coated with MOF sorbent was tested at laboratory scale under relevant conditions. Modeling of a scaled-up Microlith unit with thermal integration was also initiated using the U.S. Department of Energy's (DOE) Carbon Capture Simulation Initiative (CCSI) software, in collaboration with the University of Florida, and the model is being further validated in Phase II to show cost advantages over existing solvent-based systems. Phase II work focused on optimizing the sorbent and substrate properties; evaluating performance through durability testing with simulated flue gas; and producing a refined techno-economic analysis (TEA) model based on computational fluid dynamics (CFD) simulations and process modeling as well as a fully integrated economic analysis, including balance of plant components. Phase IIA work builds on the Phase II success to continue optimization of the sorbent for both higher capacity and long-term resistance to humidity and contaminants; support long-term durability testing at the National Carbon Capture Center on an automated small scale unit; and mature the technology for Phase III pilot tests.

During Phase II, PCI:

- Selected the (currently) best capacity commercial large-scale intent MOF and further tested it under realistic conditions and developed means for improving its stability.
- Developed means for deploying the MOF at large scale by coating it on PCI's low-pressure drop Microlith support and matured the operational map of the post-combustion carbon capture system unit in thermal swing adsorption (at 30°C) and desorption (at 80°C) to bring energy expense to 255 kilowatt-hour (kWh)/tonne of CO_2 recovered at the end of the Phase and utilization of materials with lower heat capacity. In comparison, a monoethanolamine (MEA) system requires more than 1,100 kilowatt-hour (kWh)/tonne due to steam injection.
- Developed a TEA showing the system can achieve the $30/tonne of CO_2 captured target (including compression), with $35.8/tonne projected at Phase II performance; further cost savings expected from reduction of balance of plant components; and increased efficiency to under the $30/tonne target (Phase II A target [$26/tonne], including compression).
- Developed CFD models of pilot-scale units—to be integrated with CFD package of the CCSI software.
- Assembled a small-scale MOF—Microlith unit deployed at the NCCC for initial testing with actual flue gas for model and economics validation.

Figure 1: Microlith® mesh coated with sorbent.

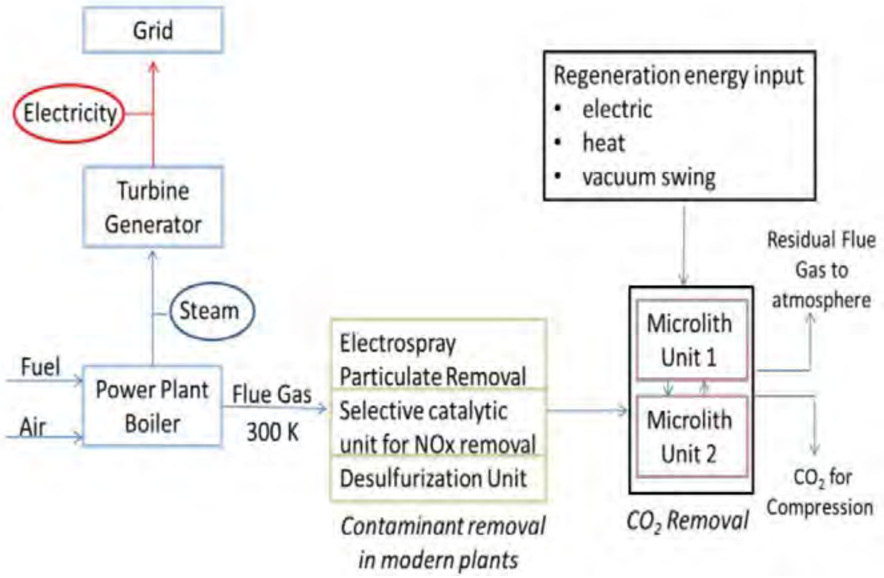

Figure 2: Process block diagram.

technology advantages

- The MOF materials have a lower regeneration energy and a lower degradation rate due to their physical adsorption capture mechanism as opposed to chemical reaction.
    - Greatly reduces boundary layer formation, with reduced pressure drop for similarly performing post-combustion carbon capture systems (pellets or monoliths-based), resulting in process intensification with corresponding reduction in post-combustion carbon capture system volume.
    - Increased mass and heat transfer coefficients and enhanced diffusion of gas in the sorbent.
    - Immobilizing the sorbent increases its lifetime by reducing attrition.
    - Modular design flexibility (e.g., planar, radial); easily scalable.
- PCI's Microlith mesh substrate supporting the MOF material has higher surface area per unit volume and much higher mass and heat transfer coefficients, as well as low-pressure drop compared to other monolith substrates or pellets, resulting in increased CO_2 capture rate and reduced regeneration energy.

R&D challenges

- Maintaining higher CO_2 loadings without affecting sorbent structure at increased production capacity.
- Identifying optimal sorbent to maximize capacity and selectivity.
- Achieving acceptable sorbent cost at large-scale production.
- Optimizing the material for long-term (thousands of cycles) operation in flue gas environment.

status

In Phase II, PCI demonstrated the Microlith-based approach to carbon capture via adsorption on MOF materials. The sorbent was stable over multiple thermal cycles and showed stability to contaminants and humidity, as well as high selectivity for CO_2 over other components of the flue gas. The system was demonstrated to have energy-saving performance due to enhanced sorption properties, heat and mass transfer, and low-pressure drop. A TEA shows potential for achieving the DOE goal of $30/tonne of CO_2 captured. PCI developed a means for deploying the sorbent at large scale by coating it on Microlith support, and matured the operational map of the post-combustion carbon capture system unit in thermal swing adsorption (at 30°C) and desorption (at 70–80°C) to bring down energy expense. PCI assembled a small-scale unit deployed at the NCCC with system shakedown and installation completed.

available reports/technical papers/presentations

Loebick, C., et al., “High-Efficiency Post Combustion Carbon Capture System,” Presented at the Phase II/Phase IIA Project Review Meeting, Pittsburgh, PA, June 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12072&filename=High-Efficiency+Post+Combustion+Carbon+Capture+System.pdf*.

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Loebick, C. and Weisman, J., “High-Efficiency Post Combustion Carbon Capture System,” Presented at the Phase I Project Review Meeting, Pittsburgh, PA, December 2017. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12074&filename=High-Efficiency+Post+Combustion+Carbon+Capture+System+(Dec+2017).pdf*.

Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Amine-Appended Metal-Organic Framework Sorbent

participant:
Lawrence Berkeley National Laboratory

project number:
FWP-FP00006194

predecessor projects:
N/A

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partners:
Mosaic Materials; Svante; Electricore Inc.

start date:
08.31.2017

percent complete:
100%

primary project goal

Lawrence Berkeley National Laboratory (LBNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, has developed a novel amine-based solid sorbent for capture of carbon dioxide (CO_2) from flue gas. The sorbent consists of a metal-organic framework (MOF) coated with alkyl amines with high affinity for CO_2. The amine-appended solid sorbents capture CO_2 in a cooperative manner through a chain reaction. The cooperative adsorption mechanism allows the sorbents to exhibit step-shaped adsorption isotherms, which allow for larger working capacities with only moderate temperature swings in contrast to the large temperature swings required by traditional amine-based sorbents. The MOF is inexpensive, as well as chemically and thermally robust. The research team identified, synthesized, and characterized amine-MOF pairs using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials were tested using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture. DOCCSS is a partnership coupling unique skill sets and perspectives of national laboratories, industry, and academic institutions, working collaboratively to facilitate discovery, synthesis, performance assessment, and functionalization of new carbon capture materials, and to accelerate the rate at which transformational processes for carbon capture are commercialized.

technical goals

- Identify, synthesize, and characterize amine-MOF pairs using existing and new computationally designed MOF and amine structures.
- Test the synthesized sorbent materials using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to impurities, and cycling performance.
- Identify the most promising sorbents with realistic potential for implementation in carbon capture.
- Field-test the MOF sorbent using actual coal-derived flue gas.

technical content

LBNL combined computational and experimental programs to synthesize and characterize amine-appended MOF sorbents for energy-efficient carbon capture. An example of the structure of an MOF with appended amines is shown in Figure 1. These MOF materials show switch-like CO_2 adsorption behavior and can be tuned to optimize working capacities under mild regeneration conditions. They exhibit step-change isotherms enabled by a cooperative CO_2 adsorption mechanism, as shown in Figure 2. This step-change isotherm allows for larger sorbent working capacities with minor temperature swings, as opposed to the large temperature swings required by traditional amine-based sorbents. The step-change isotherm shows very little hysteresis upon desorption of CO_2, and the step shifts rapidly to higher pressure with increasing temperature. Balancing CO_2 capture performance and cost is done through vigorous optimization efforts of the amine molecules and pore geometries, combining computational modeling, characterization of molecules, and experiments to evaluate CO_2 capture performance.

Diamine-appended MOFs were identified and synthesized, targeting materials showing step-change or switch-like reversible CO_2 adsorption isotherms. Computational modeling was used to identify promising amine-MOF pairs. The computational analysis and measurements of CO_2 adsorption behavior provide insight to identify second-generation materials with desired properties. The research team identified, synthesized, and characterized amine-MOF pairs using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials were tested using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture.

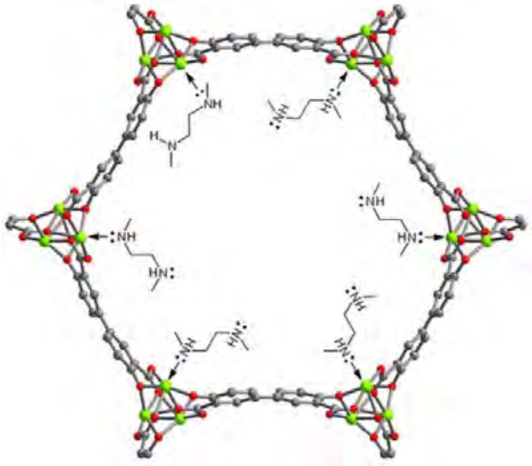

Figure 1: Example of an MOF with appended amines.

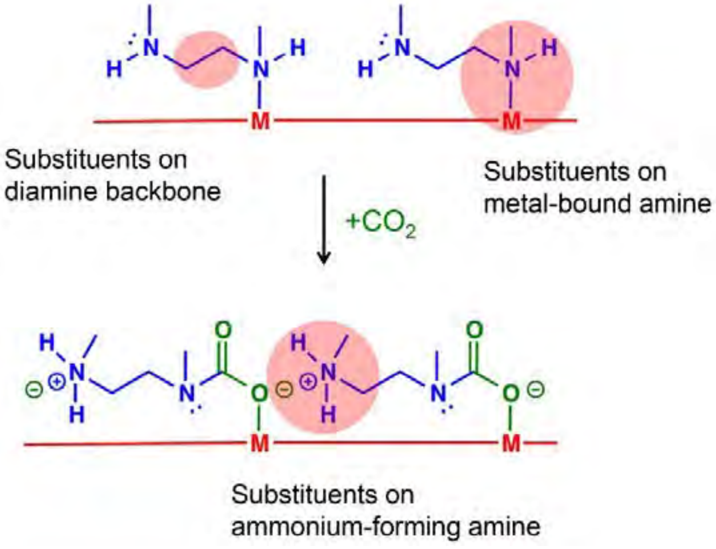

Figure 2: Cooperative CO_2 adsorption.

This project included a combined effort among several entities. LBNL was responsible for materials discovery, synthesis, and characterization. Mosaic Materials developed materials production protocols and scaled-up research and development (R&D). Sorbent production scaled-up and optimized efforts include the evaluation of four distinct steps: synthesis of the MOF, purification of the MOF to remove impurities, amination where the purified MOF is impregnated with amines, and activation where the solvent is removed. Svante and Electricore integrated the diamine-appended MOFs in a cost-effective CO_2 capture system through system development efforts. Svante performed testing of the sorbent in powder form and in a structured-bed form in their capture test units to confirm performance.

The overall effort included testing first-generation (Gen1) materials, continued development to synthesize improved diamine-appended MOF (Gen2) materials, and evaluated long-term stability, impurity effects, and alternate regeneration strategies to recover greater CO_2 capacity, culminating in field-testing using actual coal-derived flue gas.

technology advantages

- High tunability of amine-appended framework materials.
- Large working capacity due to stepped CO_2 adsorption.
- High CO_2 selectivity over nitrogen, oxygen, and water.

R&D challenges

- Large-scale and economic production of materials.
- Integration within an appropriate separation platform.
- Durability and chemical stability of these MOFs under actual flue gas.
- Reducing the regeneration cost in temperature swing.
- Steam stability and volatilization—tetraamines can significantly improve material stability due to their bidentate binding mode.
- Sulfur dioxide (SO_2)-induced degradation—extended cycling tests in the presence of these contaminants via an automated breakthrough system.
- Improving adsorbent resistance to steam stripping—identification of an adsorbent, which is better aligned with the steam regeneration methods of the VeloxoTherm™ process.
- Increasing volumetric density—investigation of alternative adsorbent forming methods, which increases sorbent density with minimal impact on capacity.
- Improving space-time yield of adsorbent synthesis—increasing the amount of adsorbent made per time and reactor volume will help lower the costs of adsorbent manufacturing.

status

LBNL identified and synthesized a Gen1 material with a 2.4 mmol CO_2/gram working capacity with a 60°C temperature swing. Mosaic Materials successfully synthesized 1 kilogram of Gen1 material that met CO_2 performance metrics and was delivered for testing at the Svante test unit.

A screening database was created to discover new MOFs with similar open metal site distance distributions to the Gen1 material, with three candidate materials of interest identified with potential for greater than 3.0 mmol/gram CO_2 uptake. One of these Gen2 materials showed a 3.6 mmol/gram working capacity with a 45°C temperature swing and an approximate regeneration energy of 2.2 MJ/kg CO_2. This Gen2 material was stable for more than 1,000 humid adsorption/desorption cycles under simulated coal-derived flue gas conditions. LBNL's work to develop a transformational technology based upon an amine-appended MOF for post-combustion CO_2 capture led to the following accomplishments:

- Synthesized and characterized a series of amine-appended MOF materials for CO_2 capture from coal flue gas—Gen1 material [chemical structure: dmpn–Mg_2(dobpdc)].
- Provided chemical insight that cannot be easily obtained using spectroscopy via density functional theory (DFT).
- Developed methods to screen through large databases for diamine-appended MOFs and accelerated the discovery of new MOF-diamine combinations.
- Demonstrated the ability to produce kilogram-scale quantities of a promising class of sorbent materials, particularly well-suited to applications in carbon capture.
- Developed the economic analysis of the production methods, which shows a path to delivering sorbent at a cost target of less than $50/kg.

- Evaluated the laminated Gen1 material in a VeloxoTherm rapid cycle temperature swing adsorption (RC-TSA) to measure key performance indicators (KPIs) and lifetime stability for coal applications. The KPI was estimated to be ca. 2 tonne-per-day/m^3 for the hot CO_2 (dry or wet) regeneration.
- Observed long regeneration times (about five to 10 times longer than the desired target [i.e., moderate KPI]). Identified that this was due to the slow heat transfer of heating the bed via a hot CO_2 purge, and pivoted toward using a steam purge, which provided much more rapid heating.
- Observed low CO_2 capacity in Gen1 laminate, which was determined to be due to the temperature rise in the bed during adsorption, as the unit is not actively cooled.
- Discovered and characterized a Gen2 material, Candidate 9, that possesses a higher CO_2 step temperature, making it more tolerant to heat rises in the bed and which exhibits unprecedented robust steam stability.
- Concluded that the Candidate 9 Gen2 MOF is superior to the Gen1 MOF material from the perspective of initial steam durability and may be suitable for preparing laminates to be tested in the VeloxoTherm process with direct steam exposure.

available reports/technical papers/presentations

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Final Briefing, Pittsburgh, PA, May 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11827&filename=Amine-+Appended+Metal-Organic+Frameworks+as+Switc-Like+Adsorbents+for+Energy-Efficient+Carbon+Capture.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2020 NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Long.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOF.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOFs.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/J-Long-LBNL-Metal-Organic-Frameworks.pdf*

A New Sorbent Process for Transformational Carbon Capture Process

primary project goal

TDA Research Inc. (TDA), in collaboration with Membrane Technology and Research Inc. (MTR), is developing a new class of sorbents to remove carbon dioxide (CO_2) selectively and with high capacity from flue gases generated from pulverized coal combustion power plants. In Phase I, TDA prepared various sorbent formulations and screened them to determine their capacity to adsorb CO_2 under representative conditions. Based on the performance results, a preliminary design of the CO_2 capture system was completed, as were cost and size estimates. The team also completed an engineering assessment to compare the system to alternative processes. In Phase II, TDA is continuing efforts to optimize the sorbent to enhance its CO_2 capacity and further improve its resistance to flue gas impurities such as moisture, sulfur oxide (SO_X), and nitrogen oxide (NO_X). Phase II also consists of scaling up the sorbent production; working with MTR to prepare polymer films, which are then formed into spiral-wound and planar modules; assessing the impact of critical process parameters at bench scale and performing a minimum of 20,000 adsorption/desorption cycles; performing process simulation work; and evaluating the techno-economic viability of the new CO_2 capture technology as a retrofit option for existing pulverized coal power plants.

technical goals

- Optimize the sorbent formulations to achieve higher CO_2 capacity and uptake rates and evaluate use of co-polymers to increase the processability of the materials into structures easily integrated into modules.
- Screen polymers and structures in bench-scale testing and prepare test modules using the best identified polymers.
- Test the modules in the TDA test apparatus using the vacuum swing adsorption (VSA) cycle and optimize operating conditions and cycle sequence.
- Complete a minimum of 20,000 adsorption/desorption cycles in presence of flue gas contaminants.
- Design a CO_2 capture process around this new material.
- Assess the techno-economic viability of the process.

technical content

TDA is developing a sorbent based on amine-functionalized resin structures for the capture of CO_2 from coal-fired power plants. In Phase I, TDA modified commercial polymeric resins with amines and tuned them for CO_2 uptake. In-house polymers were also prepared with amine functionalities and showed higher CO_2 loading than the commercial resins, along with high selectivity and kinetics. The presence of moisture enhanced the CO_2 loading. Furthermore, the TDA resins provide the flexibility to be used as coatings on engineered structures, which can reduce pressure drop and allow for the treatment of high volumes of flue gas. The sorbent regeneration occurs using a VSA cycle, and the mild vacuum conditions required results in lower regeneration energy.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Amine-Functionalized Resin Sorbent

participant:

TDA Research Inc.

project number:

SC0018682

predecessor projects:

N/A

NETL project manager:

David Lang
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principal investigator:

Gökhan Alptekin
TDA Research Inc.
galptekin@tda.com

partners:

Membrane Technology and Research Inc.

start date:

07.02.2018

percent complete:

92%

In Phase II, TDA is optimizing the sorbent formulations for improved CO_2 capacity and processability to form engineered structures capable of integration into modules. Polymer scale-up is being executed in a 50-gallon reactor system, and then the polymers are shaped into various forms, including pellets, extruded honeycomb structures, and polymer films via spin coating. Polymer beads are processed into thin sheets, which are then made into spiral-wound and planar modules by project partner MTR. Examples are shown in Figure 1.

Evaluation of the sorbent as loose granules and as modules is performed in TDA's existing VSA prototype test system (shown in Figure 2), which can treat 5 standard cubic feet per minute (scfm) of flue gas and remove up to 2.5 kilogram (kg)/hour of CO_2. Testing includes optimization of the process and the VSA cycle sequence, as well as long-term tests in the presence of contaminants. Test results are used to inform the design of a CO_2 capture process around this new polymer-based adsorbent material.

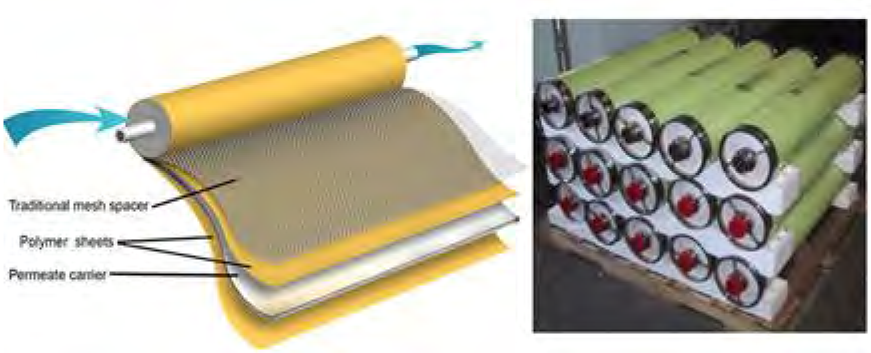

Figure 1: Example of preparation of spiral-wound modules (left) and of MTR's polymer membrane modules (right).

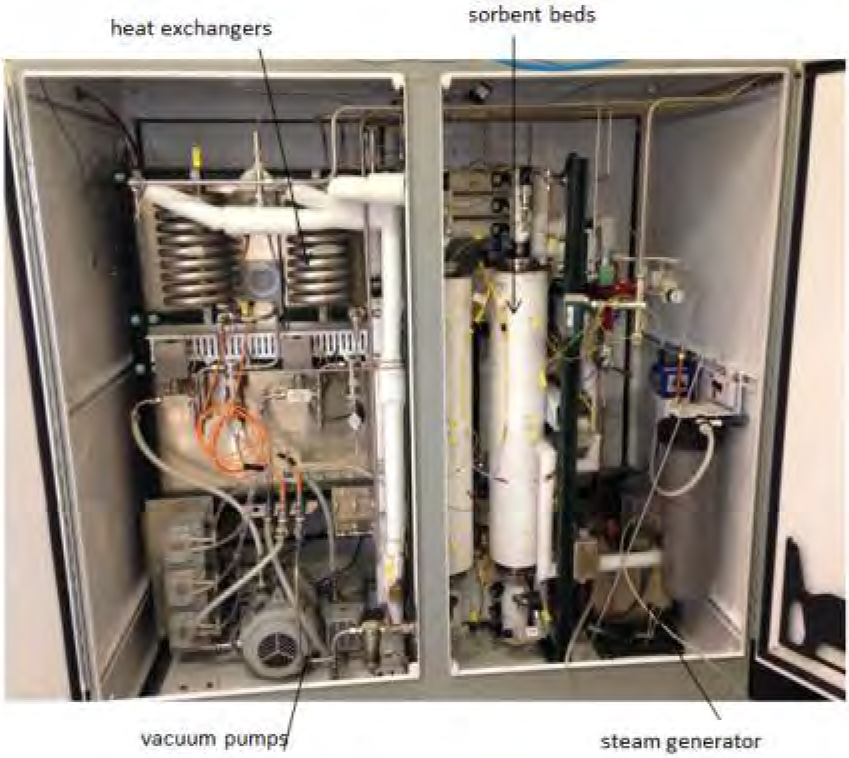

Figure 2: TDA's four-bed VSA system.

technology advantages

- Structured sorbents have potential for high CO_2 uptake with low pressure drop while treating high volumes of gas.
- Use of sorbents in a structured form instead of pellets favors use of a modular design.
- Reduced regeneration energy through a regeneration process using mild vacuum.

R&D challenges

- Preparation of the functionalized resin sorbent in engineered structures.
- Life cycle of sorbents in operational conditions with flue gas contaminants.
- Economic viability in large power plant applications due to the volume of sorbent required and cost of ancillary equipment (ductwork distribution system, vacuum pumps, etc.).

status

In Phase I, TDA has identified new polymers that can be formed into desirable structures (monoliths or planar contactors) with amine functionalities tuned for high CO_2 uptake and selectivity. Carbon dioxide capture cost was estimated to be $29.7/tonne, excluding transportation, storage, and monitoring (T&SM). In Phase II, TDA is demonstrating the efficacy of the new polymer sorbent for post-combustion carbon capture at bench-scale (2–5 kilowatt [kW]) size. Structured sorbents are being used to lower the pressure drop during CO_2 removal. TDA is finalizing the techno-economic analysis (TEA) on the viability of the new technology and final cost of captured CO_2.

available reports/technical papers/presentations

Alptekin, G. and Jayaraman, A., “A New Sorbent Process for Transformational Carbon Capture Process,” Presented at the Phase I Final Briefing/Phase II Kickoff Meeting, Pittsburgh, PA, August 2019. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12085&filename=A+New+Sorbent+Process+for+Transformational+Carbon+Capture.pdf*.

Alptekin, G, et al., “A New Sorbent Process for Transformational Carbon Capture Process,” Presented at the Phase I Project Kickoff Meeting, Pittsburgh, PA, August 2018. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12087&filename=A+New+Sorbent+Process+for+Transformational+Carbon+Capture.pdf*.

Transformational Sorbent-Based Process for a Substantial Reduction in the Cost of CO_2 Capture

primary project goal

InnoSepra LLC is developing a sorbent-based process using novel microporous materials to reduce the cost of carbon dioxide (CO_2) capture. The project includes identification of sorbent materials, process development, and lab-scale testing with simulated flue gas, culminating in bench-scale testing with actual flue gas at Technology Centre Mongstad (TCM).

technical goals

- Identify suitable materials through literature search and Monte Carlo simulations and produce/procure suitable materials for lab-scale testing.
- Complete lab-scale testing of multiple materials in simulated flue gas to determine CO_2 capture performance and downselect best materials.
- Simulate process to obtain heat and mass transfer parameters.
- Design and build the bench-scale test unit.
- Test the best identified materials on the bench-scale unit using actual flue gas at TCM.
- Perform engineering design and complete a techno-economic analysis (TEA) on the process for installation of the technology at a commercial 550-megawatt (MW) power plant to estimate CO_2 capture cost.

technical content

InnoSepra is developing a sorbent-based CO_2 capture process, utilizing physical sorbents based on microporous materials. These sorbents have low heats of adsorption (26–44 kJ/mole CO_2), high net CO_2 capacity (greater than 9 wt%), and high surface area-to-volume ratio (greater than 10 x 10^6 m^2/m^3). The combination of the process and sorbent materials provides capture performance similar to or better than amines, although needing much lower regeneration energy. The process schematic of the CO_2 capture process is shown in Figure 1. After the removal of moisture and sulfur oxides (SO_X) in a pretreatment system, the CO_2 is captured in an adsorber at 25–40°C. A high-purity CO_2 is produced during sorbent regeneration at 90–100°C. Some of the heat of adsorption is removed during the adsorption process; the remaining heat is removed during the cooling steps. Regeneration heat is supplied via low-pressure steam, as well as by utilizing other process waste heat in the system.

The first generation of the InnoSepra process using the physical sorbents was developed and tested at the bench-scale in a previous U.S. Department of Energy (DOE)-funded project (DE-FE0007948). Testing occurred at NRG Energy's Indian River Plant using actual flue gas, taken off the process after the dry flue gas desulfurization (FGD) unit, containing about 50 parts per million (ppm) sulfur dioxide (SO_2) and 10–12% CO_2, with 80–100 standard cubic feet per minute (scfm) flow rate. The adsorption test skid used at the testing at NRG is shown in

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Low Regeneration Energy Sorbent Process for CO_2 Capture from Coal-Based Flue Gas

participant:

InnoSepra LLC

project number:

FE0031722

predecessor projects:

FE0007948
SC0010208

NETL project manager:

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partners:

Main Line Engineering; Plant Process Equipment; Arizona State University

start date:

05.01.2019

percent complete:

75%

Figure 2. Eight weeks of testing was completed showing 8–10.5 wt% net CO_2 capacity, greater than 94% CO_2 recovery, and greater than 98% purity.

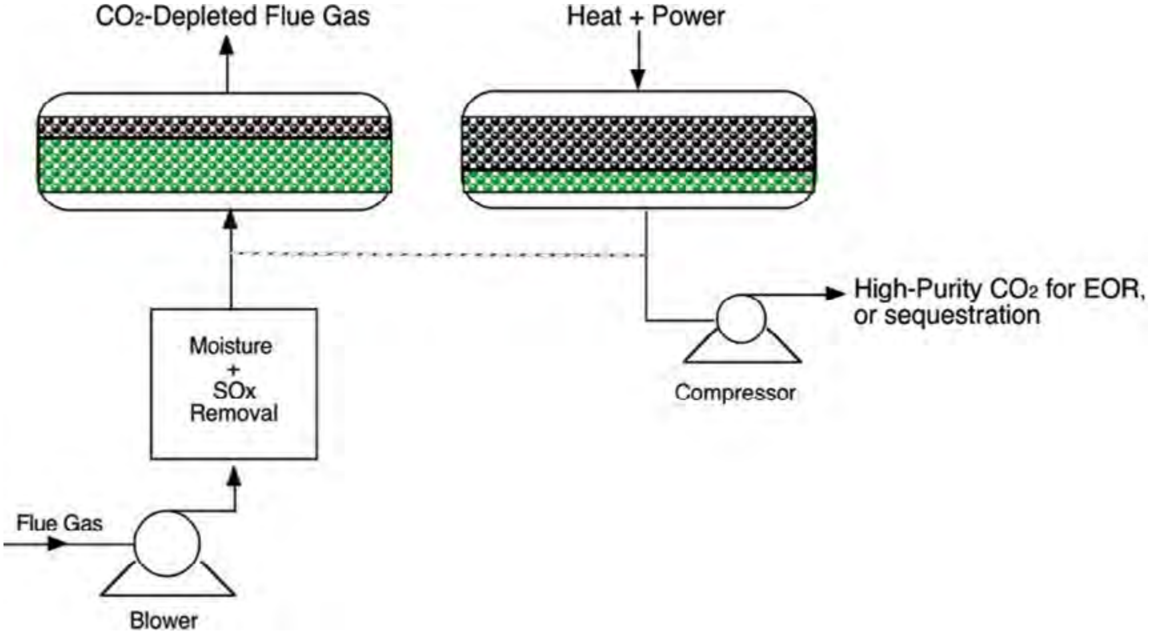

Figure 1: InnoSepra capture process schematic.

Figure 2: InnoSepra test skid used for testing at NRG Energy.

Projections based on detailed engineering evaluations show that at commercial scale, the first-generation process can reduce the power consumption for CO_2 capture by more than 40%, including CO_2 compression. There is about a 70% lower power loss due to steam extraction for the InnoSepra process compared to the amine process and approximately 48% reduction in capture cost compared to monoethanolamine (MEA).

In this project, InnoSepra is developing the second-generation process, which is simpler, with capital savings, compared to the first-generation process. In testing of the second-generation process at lab scale, an absolute energy requirement (excluding compression) of 1.6 gigajoule (GJ)/metric tonnes (MT) of CO_2 was obtained, which is 50% lower than the absolute energy requirement for an MEA-based capture process, and lower than the 2.1 GJ/MT obtained for the first-generation process of InnoSepra's technology in field testing. The lower energy requirement results from a breakthrough sorbent regeneration method. The lower absolute amount of regeneration energy coupled with lower regeneration temperature leads to a 78% lower power loss due to steam extraction compared to MEA. The key feature of the second-generation process is a significant reduction in the heating requirement (from 1.3–0.7 GJ/MT) through a combination of the sorbent selection and regeneration method. The project team is demonstrating the effectiveness of the InnoSepra sorbent-based post-combustion capture technology to achieve at least 90% CO_2 removal with greater than 98% purity. Suitable materials with at least 6 wt% CO_2 capture capacity were identified and downselected for subsequent testing in a newly constructed lab unit. Testing at lab scale, along with recently developed process simulations, helps support verification of the material properties and optimization of the process. This system shows potential to reduce the parasitic power required for regeneration by more than 65%, and the capital required by about 45%, leading to about 50% reduction in the CO_2 capture cost. A newly designed bench-scale testing unit has been designed and is being built. The unit will be shipped and tested at TCM at a scale greater than 100 scfm.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,990	1,990
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	1.5-3.0	0.5-1.5
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.79e8	1.79e8
Solid Heat Capacity @ STP	kJ/kg-K	0.96	0.96
Crush Strength	kg_f	2.9	2.9
Manufacturing Cost for Sorbent	$/kg	4.0	3.0-4.0
Adsorption			
Pressure	bar	1.15	1.1
Temperature	°C	25-32	25-32
Equilibrium Loading	g mol CO_2/kg	3.25	3.5-4.0
Heat of Adsorption	kJ/mol CO_2	38	38
Desorption			
Pressure	bar	0.3-1.0	0.3-1.0
Temperature	°C	100	90-110
Equilibrium CO_2 Loading	g mol CO_2/kg	1.0-1.5	1.0-1.5
Heat of Desorption	kJ/mol CO_2	38	38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed/cyclic	
Flue Gas Flowrate	kg/hr	2,320,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 99 1.0	
Adsorber Pressure Drop	bar	0.14	0.10
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	336	

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	35	30

Cost of Carbon Avoided	\$/tonne CO_2	39.5	31.5
Capital Expenditures	\$/ MWhr	53	45
Operating Expenditures	\$/ MWhr	14	12
Cost of Electricity	\$/MWhr	94	88

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Contaminant Resistance – Under normal operation, the sorbent is not irreversibly damaged by any contaminant in the flue gas. If substantial quantities of SO_2 are present in the feed to the CO_2 adsorption section, the sorbent may require higher than normal regeneration temperature to restore performance.

Sorbent Attrition and Thermal/Hydrothermal Stability – The process design protects the adsorbent from moisture and potential hydrothermal degradation. If moisture should break through onto the adsorbent, the adsorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300°C.

Flue Gas Pretreatment Requirements – No special flue gas pretreatment is required. A conventional FGD and a direct contact cooler (DCC) are sufficient for normal process operation.

Sorbent Makeup Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between five and 10 years. An adsorbent life of five years has been assumed to estimate the makeup requirements.

Waste Streams Generated – Except for the sorbents loaded with flue gas components, SO_X and mercury (Hg), no other waste streams are generated in the process. These can be disposed of as per current power plant practices for materials loaded with SO_X and Hg.

Process Design Concept – The commercial process configuration is shown in Figure 3. The adsorption equipment is modular in nature and five adsorption skids are needed for a 550-MW power plant. The rest of the process equipment, such as the feed blower, DCC, and the CO_2 compressor, is very similar to the amine process.

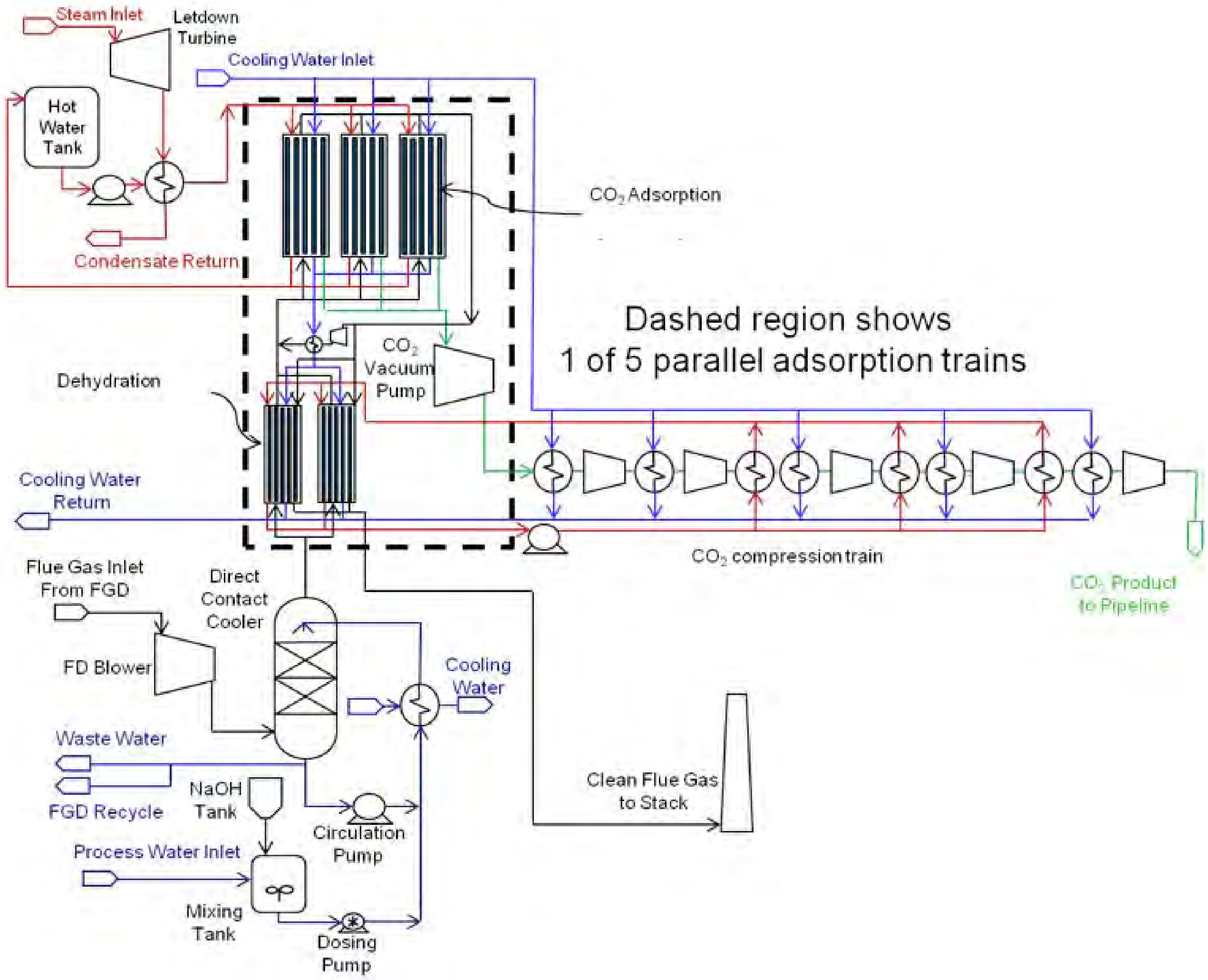

Figure 3: Commercial process configuration.

Proposed Module Design – The CO_2 capture modules will be designed to capture CO_2 from a 550-MW pulverized coal power plant. Multiple modules will be used to minimize field fabrication and maximize offsite fabrication. The separation skid will consist of a feed preparation section (flue gas compression and cooling), the CO_2 adsorption section (removal of impurities, CO_2 adsorption, and desorption), and the CO_2 compression section.

technology advantages

- The physical sorbents have a low heat of adsorption (approximately 0.8 GJ/MT).
- Combination of lower absolute amount of heat needed and lower steam extraction temperature leads to a 78% lower power loss compared to MEA.
- The process can produce high-purity CO_2 (greater than 98%) and recovery (greater than 90%).

- The estimated absolute energy required for the process, excluding compression, is 1.6 GJ/MT of CO_2, less than half of the absolute energy requirement for an MEA-based process.
- Regeneration energy can be utilized at approximately 110°C, compared to greater than 170°C for amines.
- The process has a projected capture cost below $30/MT CO_2, excluding transportation, storage, and monitoring (TS&M) costs.

R&D challenges

- Heat management during both adsorption and regeneration.
- Maintaining heat transfer rate upon scale-up.
- Assuring effective moisture and contaminant removal from the flue gas prior to adsorption to prevent decrease in sorbent performance over time.

status

The project's first budget period has been completed, and the second budget period is in progress. Suitable materials were identified, downselected, and tested in a constructed lab-scale unit. Process models have been developed, and a detailed engineering design was completed for a bench-scale unit to be tested at TCM. Fabrication of the bench-scale unit will be followed by shipping to and testing at TCM, with a field-testing report and analysis to be subsequently completed.

available reports/technical papers/presentations

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jain.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Budget Period 1 Meeting, Pittsburgh, PA, April 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10721&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Project Kickoff Meeting, Pittsburgh, PA, September 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10719&filename=Transformational+Sorbent-Based+Process+for+a+Substantial+Reduction+in+the+Cost+of+CO2+Capture.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/R-Jain-InnoSepra-Cost-Reduction-Capture.pdf*.

Advanced Structured Adsorbent Architectures for Transformational Carbon Dioxide Capture Performance

primary project goal

Electricore, teamed with Svante and Susteon, is optimizing Svante's transformational VeloxoTherm™ Technology via the development and field testing of an advanced structured adsorbent bed (SAB) to enhance its performance and lifetime. The project team will select, synthesize at large scale, and characterize tailored solid adsorbents, optimize the SAB laminate and Rotary Adsorption Machine (RAM) contactor structure and geometry, develop a final process cycle using process simulations and state-of-the-art modelling, and complete dynamic bench-scale testing with natural gas-fired boiler flue gas and cement plant flue gas.

technical goals

- Synthesis at large scale (greater than 500 kg) of tailored solid adsorbents, including a MOF.
- Optimize the design and fabrication of the segmented bed with, possibly, different geometries to optimized sorbent utilization and keep low pressure drop and laminar flow.
- Optimize the rapid cycle temperature swing adsorption (RC-TSA) process to increase the CO_2 capture efficiency of two different sorbents in the same cycle.
- Develop a segmented bed configuration for both low (less than 12%) and high (greater than or equal to 12%) CO_2 concentration.
- Build and test segmented beds using multi-bed field demonstration units with flue gas from a natural gas-fired boiler (low CO_2 concentration) and from a cement plant (high concentration).
- Assess the techno-economic performance of the technology integrated into a 550-megawatt-electric (MWe) coal-fired power plant.

technical content

The project team is developing an advanced structured adsorbent bed geometry and rotary contactor architecture including segmented layers bed for post-combustion CO_2 capture in order to develop Svante's Mark II VeloxoTherm technology. Two configurations of segmented beds will be explored: low concentration (less than 12% CO_2) and high concentration (greater than 12% CO_2). The low-concentration configuration will be tested in-house in a multi-bed process demonstration unit (PDU) to demonstrate key performance indicators (KPIs), such as recovery, product purity, regeneration energy, lifetime, and the integrated system's productivity. The second configuration of segmented beds, for higher CO_2 concentration, will be tested at a 1-tonne-per-day (TPD) unit at an industrial site (cement plant) to provide bench-scale validation of performance in an industrial setting.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

Structured Sorbent Beds

participant:

Electricore Inc.

project number:

FE0031732

predecessor projects:

N/A

NETL project manager:

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principal investigator:

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partners:

Svante Inc.; Susteon, Inc.

start date:

05.01.2019

percent complete:

80%

The segmented bed configuration combines two or more sorbents in the direction of the sorption. As a result of the counter-flow of the steam and flue gas streams, and the fast process cycle (less than 60 seconds), temperature and relative humidity (RH) conditions are different throughout the length of the bed with some areas suffering more from oxidation and some areas with higher RH, which could decrease the CO_2 capacity of a metal organic framework (MOF) sorbent. The segmented bed concept permits the use of the optimal sorbent for the given local condition (Figure 1). The advantage of the segmented bed is the ease of retrofitting to existing plants design and to extend the lifetime and performance.

The process and segmented bed design needs to be optimized to efficiently use the same process for both the adsorption, desorption, and regeneration, keeping equivalent CO_2 capacity for each sorbent section, minimizing the flow resistance and loss of laminar at the interface and ease of manufacturing. Overall, this process has potential for increased sorbent CO_2 capacity, increased lifetime, and reduced steam demands.

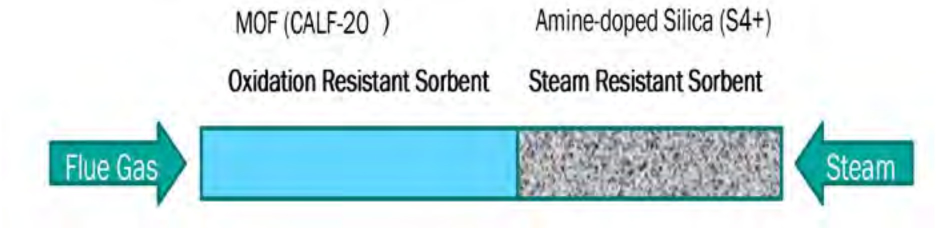

Figure 1: Typical example of the segmented bed concept design.

Optimization of the segmented bed geometry and process is being tested in a single-bed sorbent test using simulated coal-fired flue gas in the Svante Variable Test Station (VTS) shown in Figure 2a, at a scale of approximately 1–10 kg of CO_2/day captured. Afterwards, the Mark II advanced structure will be tested using the VeloxoTherm process with a multi-bed testing station. The low-concentration series will be tested in the Svante rotating adsorption machine in the PDU that is coupled with a natural gas-fired boiler for testing at a maximum of 10 kg of CO_2/day captured. The high-concentration series will be tested in the 1-TPD field unit running flue gas from a Lafarge cement plant in Richmond, Canada.

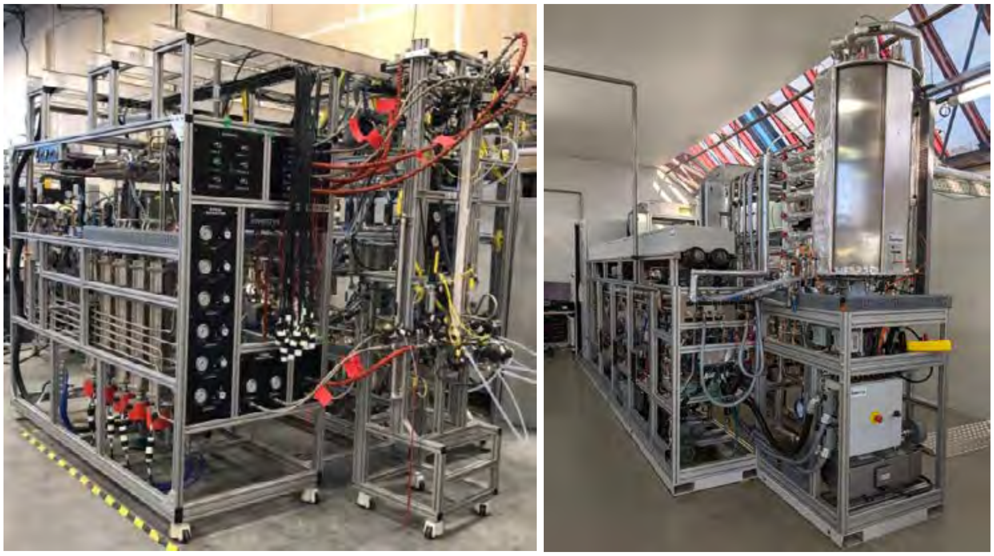

Figure 2: The variable test station at Svante (VTS, left) and the Process Demonstration Unit (PDU, right).

Figure 3: CO_2MENT field Unit (1 TPD) at a Lafarge cement plant in Richmond BC showing the pre-treatment system and capture plant (left) and the RAM showing the beds (right).

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	350-380	350-380
Bulk Density	kg/m^3	N/A	N/A
Average Particle Diameter	mm	0.31-0,35	0.31-0.25
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density	m^2/m^3	2,300-2,500	2,300-2,500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO2)	g mol CO_2/kg	1.7-1.8	1.9-2.0
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			
Pressure	bar	0,8-1.0	0.8-1.0
Temperature	°C	110-120	110-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.4-0.5
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving beds	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95	95 150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loading is mass of dry sorbent measured with 20% CO_2 in nitrogen (N_2) mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas, assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) sulfur oxide (SO_X) and nitrogen oxide (NO_X).

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional direct contact cooler (DCC). Chemical scrubber to decrease contaminants and particulates (SO_X less than 10 ppm; nitrogen dioxide [NO_2] less than 10 ppm; dust less than 20 mg/Nm^3).

Sorbent Make-Up Requirements – Five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site-specific	Site-specific
Capital Expenditures	\$/TPD	70,000-80,000	60,000-70,000
Operating Expenditures	\$/tonnes CO_2	26-28	20-23
Cost of Electricity	\$/tonnes CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced, including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5–6 cents per kilowatt-hour (kWh).

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the techno-economic analysis (TEA) from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs of the capture unit compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).
- Usage of ultra-stable solid sorbent prevent toxic emission.
- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.
- Svante unique laminate technology unlocks to use of different sorbents for performance or lifetime optimization (segmented bed concept).

R&D challenges

Tuning the two sorbents—materials, coatings, and manufacturing—to work in synergy within the same process conditions.

status

The project team successfully built a dual-channel parallel film heat exchanger with adsorbent and an extremely low mass flow separator (bi-layered concept). They demonstrated the effectiveness of heat transport between the A and B sides. The project team also demonstrated fast indirect regeneration of sorbent across the barrier layer and found a significant reduction (~35%) in the steam ratio by avoiding excess steam addition. However, the increase in complexity of the manufacturing of the bi-layered beds combined with the required modification of the actual RAM is a drawback. The use of the segmented bed concept optimizing the lifetime or regeneration energy of a bed by the optimization of the sorbent choice for the local condition in a Svante bed is a highly promising Mark II design. The target KPIs at the VTS level were clearly identified for both low- and high-CO_2 concentration segmented bed concept. The Electricore team will start long-term testing using the VeloxoTherm RAM field demonstration unit. Svante was able to scale-up MOF manufacturing to the tonnes scale with the help of the BASF chemical company.

available reports/technical papers/presentations

Jelen, D and Hovington, P. "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jelen.pdf*.

Jelen, D and Cizeron, J. "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," 2020 NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Jelen.pdf*.

Jelen, D. "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," Budget Period 1 Review Meeting, Pittsburgh, PA, June 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10743&filename=Advanced+Structured+Adsorbent+Architectures+for+Transformative+CO2+Capture+Performance.pdf*.

Jelen, D. "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/D-Jelen-Electricore-Adsorbent-Architectures.pdf*.

Jelen, D. "Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance," Kickoff Presentation, Pittsburgh, PA, August 2019. *https://netl.doe.gov/projects/plp-download.aspx?id=10744&filename=Advanced+Structured+Adsorbent+Architectures+for+Transformative+CO2+Capture+Performance.pdf*.

Transformational Sorbent System for Post-Combustion Carbon Capture

primary project goal

TDA Research, partnered with University of Alberta, University of California Irvine, and the Wyoming Integrated Test Center (ITC), is developing a transformational sorbent system for post-combustion carbon dioxide (CO_2) capture capable of capturing more than 90% of the CO_2 emissions from a coal-fired power plant and recovering CO_2 at 95% purity with a cost of electricity 30% lower than an amine-based system. TDA's system uses a novel, highly stable, high-capacity CO_2 sorbent in a vacuum/concentration swing adsorption (VCSA) process that uses a single-stage vacuum pump with low auxiliary load. The sorbent regeneration comprises two steps: (1) a vacuum to recover the CO_2 and (2) a purge using boiler air intake, subsequently feeding the CO_2-laden air to the boiler. The technology provides a cost-effective solution for controlling CO_2 emissions from existing coal-fired power plants. The low heat of adsorption of CO_2 and the use of a VCSA process that eliminates any steam purge results in reduced energy input for sorbent regeneration. The radial outflow sorbent reactor beds can be constructed into modules that can be added together, allowing for easy scale-up.

technical goals

- Optimize the sorbent formulation.
- Assess impact of flue gas contaminants (sulfur dioxide [SO_2], nitrogen oxide [NO_x], hydrogen chloride [HCl]).
- Scale-up sorbent production.
- Complete long-term sorbent cycling experiments at bench scale using simulated flue gas.
- Design and construct a prototype system with fixed-bed radial flow reactors.
- Design the VCSA cycle sequence.
- Perform field-testing in a prototype test unit using actual flue gas for a minimum of 4,000 hours.
- Prepare a high-fidelity techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

TDA Research is developing a high-capacity sorbent for CO_2 capture in a system that uses a novel adsorption cycle scheme. TDA's metal organic framework (MOF) sorbent has very high CO_2 uptake, high CO_2 selectivity over nitrogen (N_2), and a relatively low energy requirement for regeneration. The process, shown in Figure 1, includes sorbent that operates at approximately 50°C during adsorption under mild vacuum (~0.2–0.3 atmosphere [atm]). The regeneration occurs in a two-step process, using vacuum to recover the CO_2 and a purge using the boiler intake air, which then feeds the CO_2-laden air back to the boiler. This approach generates a flue gas that is rich in CO_2, thereby benefiting the adsorption of the CO_2 on the sorbent while allowing use of a practical, single-stage vacuum pump with a low auxiliary load.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Metal Organic Framework-Based Sorbent System

participant:
TDA Research Inc.

project number:
FE0031734

predecessor projects:
N/A

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TDA Research Inc.
galptekin@tda.com

partners:
University of California Irvine;
University of Alberta;
Wyoming Integrated Test Center

start date:
06.01.2019

percent complete:
67%

The project team is designing a fixed-bed radial flow reactor-based test unit for field-testing at a project partner host site with actual coal-derived flue gas to show the performance of their CO_2 capture system. TDA's radial flow contactor increases the viability of using sorbents in fixed beds for post-combustion capture by reducing the pressure drop through the beds and allowing for rapid regeneration of the sorbent. The radial flow reactor configuration allows for use of multiple modular beds for ease of scale-up to large-scale processes.

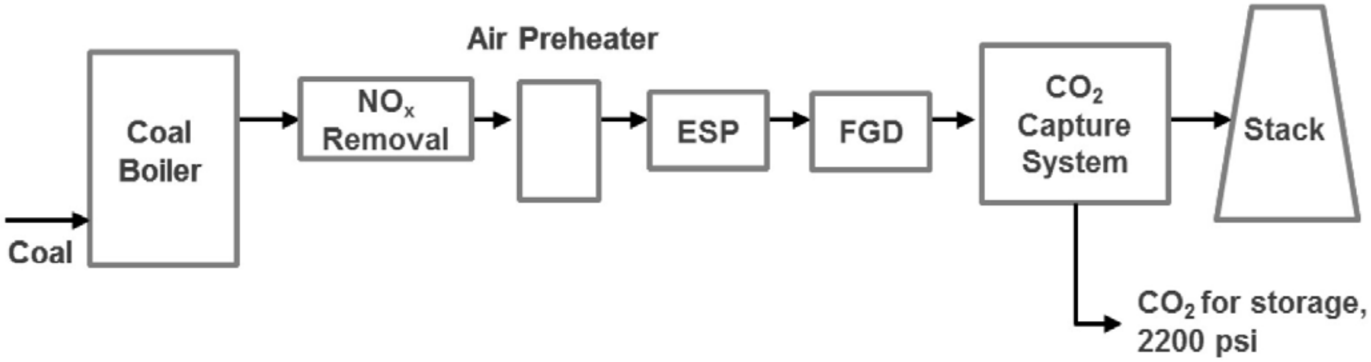

Figure 1: Schematic of TDA's CO_2 capture system.

TDA Research is optimizing sorbent performance through lab-scale experiments and using computational modeling to show the technical merit of both the sorbent and the capture process. The impacts of flue gas contaminants, including SO_2, NO_X, and HCl, on sorbent performance are being evaluated. The project team will also design and construct the prototype system, design the VCSA cycle, optimize the process design, and complete a detailed cost analysis to compare this process technology against amines. Evaluations using the prototype test unit will be completed first with simulated flue gas in the lab and then at the Wyoming ITC with actual coal-based flue gas, followed by optimization of the cycle design, finalization of the process design, and completion of an engineering analysis to fully assess the techno-economic viability of the process.

technology advantages

- Very high CO_2 uptake (2–3 mmol/g) at 0.15–0.20 bar CO_2 partial pressure.
- High CO_2 selectivity over N_2.
- Relatively low energy input requirement for sorbent regeneration.

R&D challenges

- Minimizing the loss in adsorption capacity due to the sorbent pelletization process.
- Designing the sorbent to maintain stability and life in the presence of moisture.
- Maintaining the low vacuum and purge requirements for the process upon scale-up.

status

TDA Research MOF synthesis improvements have produced space yield improvements of 10–15X and time yield improvements of 5–8X. The reactor was equipped to perform MOF synthesis, filtration/rinsing, and drying/devolatilization, all sequentially in the same reactor. A classified area is designed and built to handle the equipment and solvents required for MOF processing. TDA employed multiple fixed-bed adsorption systems to carry out adsorption breakthrough and adsorption/desorption cycle tests. Scale-up testing from 1–22 L flask and to 180 L Hastelloy reactor will occur in Budget Period 2 (BP2). TDA Research demonstrated a high working capacity in excess of 5 wt%. CO_2 at approximately 15 vol%. CO_2 and approximately 2.5 wt% CO_2 at 4 vol% CO_2. TDA Research also demonstrated how temperature and humidity levels have limited impact on sorbent's working capacity. Higher temperatures resulted in lower working capacity. There was no significant impact in the presence of humidity up to 65%. Stable working capacity was also demonstrated in the presence of flue gas contaminants such as NO_X and sulfur oxide (SO_X). The TEA indicated the total cost of the CO_2 capture system, including flue gas treatment, is $207.8 Million ($378/kW), and the cost of CO_2 capture is approximately

$37/tonne, which meets the U.S. Department of Energy's (DOE) current target of less than $40/tonne at less than $450 Million.

available reports/technical papers/presentations

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_TDA.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," Budget Period 1 Review Meeting, Pittsburgh, PA, January 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=10759&filename=Transformational+Sorbent+System+for+Post-Combustion+Carbon+Capture.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," 2019 Carbon Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Next-Gen-Sorbent.pdf*.

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," Kickoff Presentation, Pittsburgh, PA, August 2019. *https://netl.doe.gov/projects/plp-download.aspx?id=10758&filename=Transformational+Sorbent+System+for+Post-Combustion+Carbon+Capture.pdf*.

Transformational Molecular Layer Deposition, Tailor-Made, Size-Sieving Sorbents for Post-Combustion CO_2 Capture

primary project goal

Rensselaer Polytechnic Institute (RPI) is developing a transformational molecular layer deposition (MLD), tailor-made, size-sieving sorbent/pressure swing adsorption (PSA) process (MLD-T-S/PSA) that can be installed in new (or retrofitted into existing) pulverized coal (PC) power plants for carbon dioxide (CO_2) capture. The project's technical activities include mathematical modeling, development of MLD tailor-made sorbents, MLD sorbent design, construction of an MLD-T-S/PSA system, and techno-economic analysis (TEA). The project team includes the University of South Carolina (USC), Gas Technology Institute (GTI), Trimeric Corporation, and the National Carbon Capture Center (NCCC). USC will conduct sorbent performance testing, PSA process optimization, and system design and construction. GTI will evaluate the influence of impurities on sorbent performance, construct a testing skid at USC, and transport the testing skid to the National NCCC in Wilsonville, Alabama, for field testing. Trimeric will perform the TEA based on the NCCC test results.

technical goals

- Generate tailor-made, size-sieving sorbents by using MLD to coat sorbents.
- Identify promising sorbent materials through computational screening.
- Optimize MLD process to develop sorbents with high CO_2 adsorption capacity and stability in the presence of water vapor.
- Perform single-bed testing and simulation with the developed sorbents.
- Identify allowable contaminant levels for sorbents by further single-bed testing and simulation.
- Design PSA cycle schedule tailored to best MLD-modified sorbent.
- Design and construct MLD-modified sorbent/PSA skid system.
- Test skid system under simulated flue gas and actual flue gas conditions.
- Perform a TEA of the process integrated with a 550-megawatt-electric (MWe) power plant.

technical content

RPI, in collaboration with USC and GTI, is developing a process that integrates transformational, tailor-made, MLD-modified sorbents with a novel PSA process concept to achieve U.S. Department of Energy (DOE) CO_2 capture performance and cost goals. RPI has developed sorbents with CO_2/nitrogen (N_2) selectivity as high as 130—much higher than state-of-the-art commercial sorbents, such as 13X zeolite, with similar CO_2 capacity under similar adsorption conditions—enabling achievement of 95% CO_2 purity in a single stage PSA for CO_2 capture from flue gas. The sorbents are coated with an inorganic material to achieve pore misalignment, which allows for fine-tuning the pore mouth size on the surface of sorbents (Figure 1). Using MLD, a vapor phase deposition technique utilizing self-

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Size-Sieving Sorbent Integrated with Pressure Swing Adsorption

participant:
Rensselaer Polytechnic Institute

project number:
FE0031730

predecessor projects:
N/A

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partners:
University of South Carolina; Gas Technology Institute; Trimeric Corporation

start date:
10.01.2019

percent complete:
82%

limiting surface reactions, the external surface of the base sorbent is uniformly coated by ultrathin (less than 20 nanometers [nm]) microporous coatings. A wide range of porous materials (zeolites, activated carbon, and metal-organic frameworks [MOFs]) in different forms (powder or pellets) can be used directly as the base material for MLD coating, and the pore mouth size can be precisely designed by controlling the coating layer composition and thickness, as well as the thermal treatment conditions. The MLD-modified sorbents provide precise pore mouth size control in the range of 0.01 nm, which is crucial for achieving highly selective separation of CO_2 from N_2, as illustrated in Figure 2. MLD treatment results in minimal loss to the CO_2 adsorption capacity of the base sorbent.

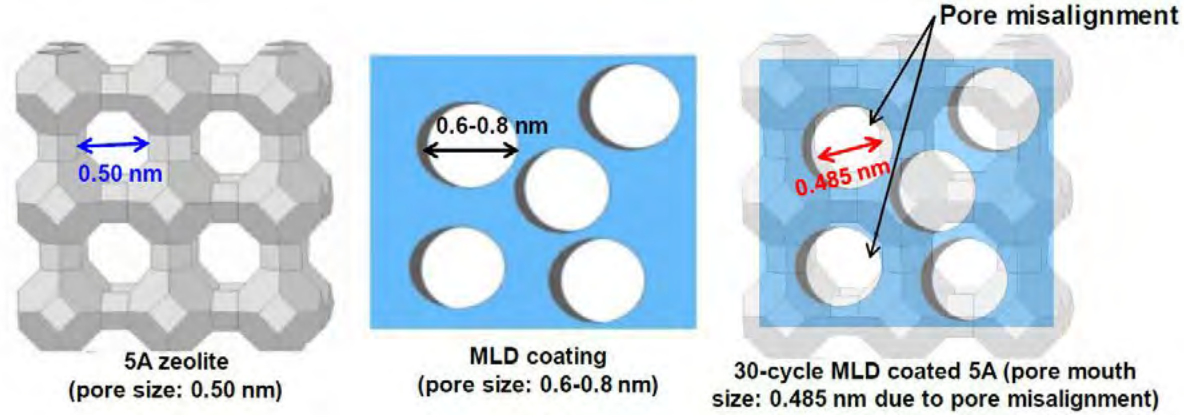

Figure 1: Schematic of pore misalignment for fine-tuning pore mouth size of sorbents.

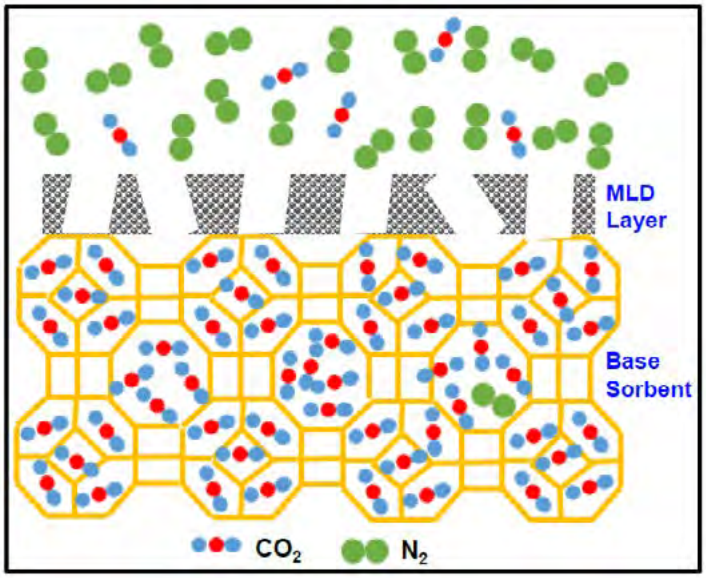

Figure 2: High CO_2/N_2 selectivity achieved by size-sieving for the MLD tailor-made sorbent.

Early studies on the pore misalignment concept show that 5A zeolite with and without MLD coatings have almost identical surface areas (343.5 ± 8.3 m^2/g) and micropore volume, suggesting that the coatings are only on the external surface and the internal cavity of the zeolite is maintained (Figure 3). Furthermore, the effective pore size of the treated 5A zeolite can be precisely controlled by the number of MLD cycles. Preliminary experiments on MLD-coated 13X zeolite show that almost no N_2 is adsorbed, suggesting a molecular sieving mechanism, and indicate a reduction in the heat of adsorption of CO_2. The sorbent and process parameters are provided in Table 1. In addition to 5A and 13X zeolites, other microporous sorbents have the potential to achieve high CO_2 adsorption capacity and CO_2/N_2 selectivity with MLD modification.

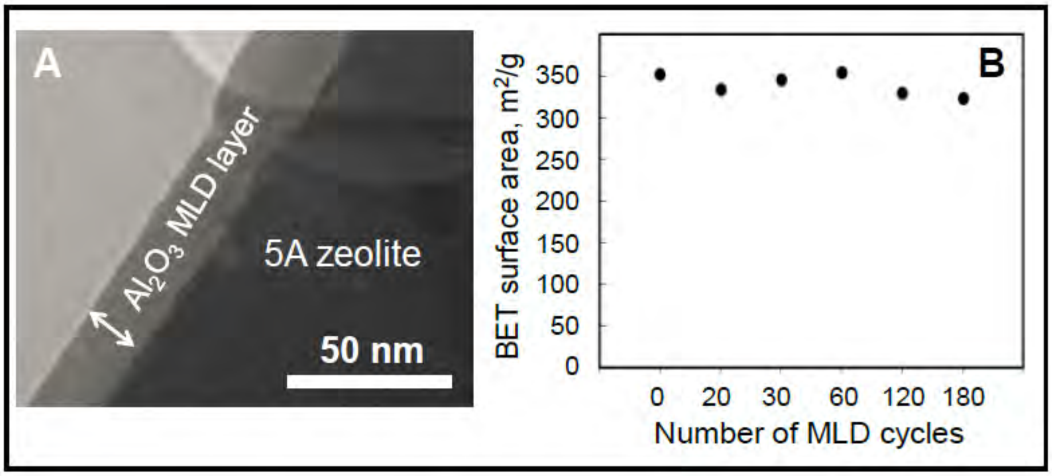

Figure 3: Characterization of MLD-modified 5A zeolite: (A) transmission electron microscopy (TEM) image of 5A zeolite with 60 cycles of aluminum oxide coating; (B) BET surface area of 5A zeolite with different cycles of MLD.

USC has recently developed a proprietary PSA cycle schedule concept for CO_2 capture from flue gas that involves the use of fewer number of beds than employed in their previously DOE-supported project DE-FE0007639, thereby reducing the CO_2 capture cost significantly. The number of required beds is reduced from 240 to 48 (i.e., six, eight-bed PSA systems operating in parallel) for the MLD-coated sorbent/PSA process integrated into a 550-MWe power plant. Figure 4 shows a diagram of the process, including identification of the numbered streams. The flow sheet incorporates desiccant wheels for water vapor removal upstream of the PSA process that are regenerated by a simple concentration swing with the light product from the PSA system and ambient air without the use of any heating. The dry light product (~2.4 mol% CO_2) produced by the PSA system is used to regenerate Dryer 2, and slightly compressed ambient air is used to regenerated Dryer 1. A reflux compressor produces a concentrated recycle stream containing approximately 83 mol% CO_2, facilitating the production of greater than 95 mol% CO_2 in the final CO_2 product. The system is uniquely designed with six adsorption beds being fed simultaneously, while two beds are being regenerated. This ensures low pressure drop during the feed step with a beaded adsorbent for large flow rate feed streams, allowing for the use of fewer number of adsorption beds in the PSA system since the adsorption bed height can be increased without a pressure drop penalty.

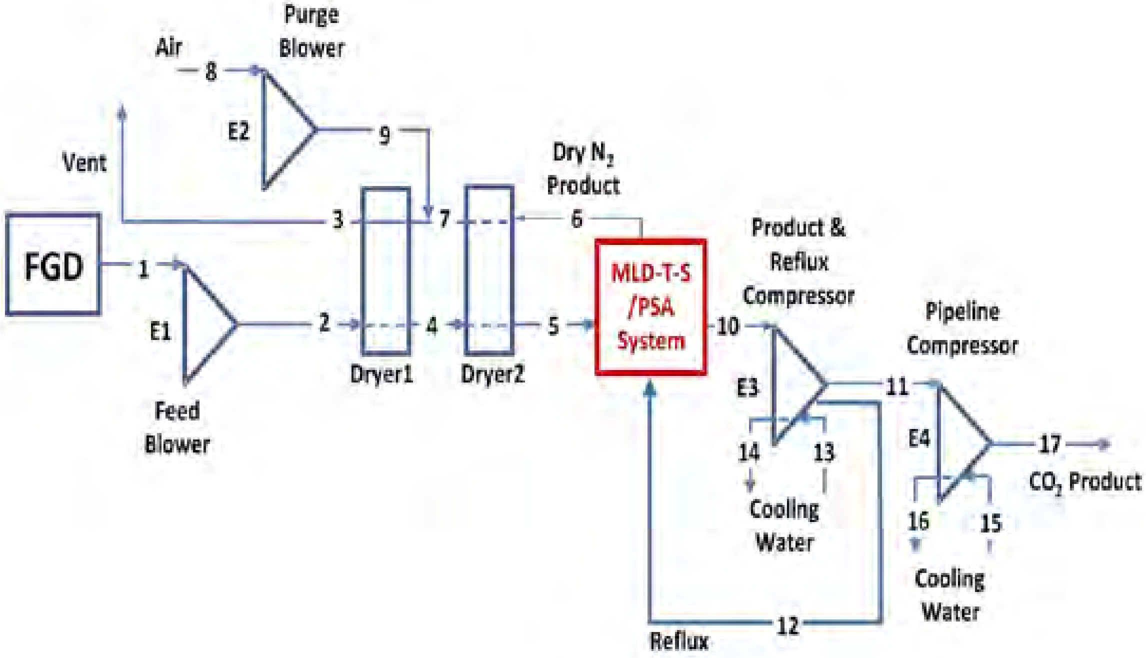

Figure 4: USC's PSA process flow diagram integrated with the MLD sorbent/PSA system.

USC's dynamic adsorption process simulator (DAPS) has been used to design a hypothetical MLD-treated sorbent/PSA system, showing a 6% reduction in separation energy when using MLD-coated 13X zeolite compared to commercial 13X. Preliminary TEA results compared to the DOE/National Energy Technology Laboratory (NETL) Base Case 9 (subcritical PC plant without CO_2 capture) and Base Case 10 (subcritical PC plant with amine scrubbing) are shown in Figure 5, indicating that the MLD-treated sorbent/PSA system can achieve 90% CO_2 capture rate with 95% CO_2 purity with a cost of \$28/tonne CO_2.

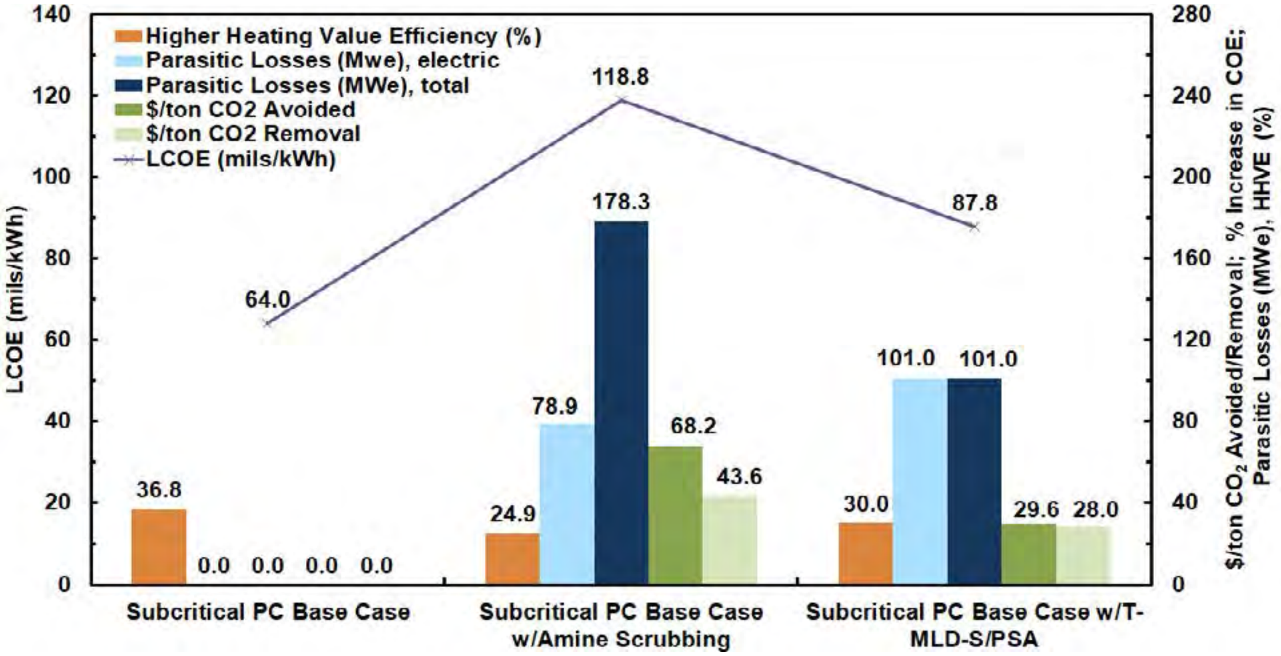

Figure 5: Comparison of the cost of CO_2 capture between DOE/NETL Base Case 9 (subcritical PC plant without CO_2 capture), Base Case 10 (subcritical PC plant with amine scrubbing), and the MLD-coated sorbent/PSA process.

technology advantages

- High CO_2/N_2 selectivity (greater than 130), enabling a 95 vol% CO_2 purity to be achieved in a single stage for a typical coal flue gas containing 12–15 vol% CO_2.
- Uses low-cost commercial sorbents as base material.
- Metal and organic precursors required to form the coating materials are low cost.
- MLD is comparable to commercially available atomic layer deposition technology and suitable for roll-to-roll manufacturing.
- MLD tailor-made sorbent technology allows for reduced vacuum level and reduced light reflux flow during regeneration, thereby reducing the size and energy required by the product and reflux vacuum pump.
- Advanced sorbent fabrication procedure reduces manufacturing cost.
- Low pressure drop during feed step leads to use of fewer adsorption beds in PSA cycle, reducing capital costs.
- Compact, stand-alone, and modularized system design, reducing upfront installation costs and footprint.
- Serves as a platform for CO_2 capture from both coal-fired and natural gas-fired power plants.

R&D challenges

- Precise control of the MLD coating properties to form appropriate pore misalignment for molecular sieving.
- Degradation of MLD sorbent performance in the presence of flue gas contaminants.
- Lower CO_2 purity when integrating MLD sorbent with the new PSA cycle.

status

The project team is using MLD to apply microporous coatings of less than 30 nm thickness on base sorbent material. Computational screening of various sorbent materials is being used to identify the sorbents for this technology. DAPS is being used to design the PSA system based on commercial 13X zeolite to establish baseline performance. A unique 100 Hz volumetric frequency response (VFR) was designed, constructed, and became operational at USC. This system will be used to measure mass transfer rates and mechanisms in virgin and MLD-modified zeolite beads. In addition, a unique six-bed PSA system was designed, constructed, and became operational at USC. It was modified and upgraded to operate with two feed or two light reflux beds. Start-up and troubleshooting have commenced, with preliminary results currently being evaluated. Molecular Dynamics (MD) simulations were used to identify how the transport at the MLD/base sorbent interface can enhance the overall selectivity. Future simulations that include modifications within the base sorbent will expand the design space of modified materials. MLD was shown as an effective technology to modify 13X zeolite and optimized its properties relevant to PSA. The optimized sorbent showed almost no loss in CO_2 working capacity and approximately a doubling of CO_2/N_2 selectivity under relevant PSA conditions. Simulations with DAPS have shown that it may be possible to have a two-unit, 10-bed, 13-step Vacuum Swing Absorption (VSA) cycle (i.e., a 20-bed VSA system when using a 9-mm-diameter 13X zeolite bead); a unique scaling procedure was developed to meet pressure drop requirements and bed design constraints while minimizing the total surface area of the beds required in the VSA system.

available reports/technical papers/presentations

Underhill, P., Ritter, J., Miao, Y. “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Underhill.pdf*.

Yu, M., et al. “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” Kickoff Meeting Presentation, Pittsburgh, PA, November 2019. *http://netl.doe.gov/projects/plp-download.aspx?id=10733&filename=Transformational+Molecular+Layer+Deposition+Tailor-Made+Size-Sieving+Sorbents+for+Post-Combustion+CO2+Capture.pdf*.

Yu, M., et al. “Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Yu-RPI-Tailor-Made-Sorbents.pdf*.

Bench-Scale Testing of Next-Generation Hollow-Fiber Membrane Modules

primary project goals

Air Liquide developed a novel polyimide-based membrane material, PI-2, for application in their hybrid process that combines cold membrane operation with cryogenic separation to reduce the overall cost of capturing carbon dioxide (CO_2) from the flue gas of coal-fired power plants. The focus of the project was to advance the high CO_2 permeance PI-2 material to commercial-scale, 6-inch bundles for testing with actual flue gas in a 0.3-megawatt-electric (MWe) test unit at the National Carbon Capture Center (NCCC).

technical goals

- Design and manufacture 4-inch PI-2 bundles reaching greater than 90 normal meters cubed per hour (Nm^3/hr) feed at 90% CO_2 recovery and greater than 58% CO_2 purity.
- Identify other hybrid processes with possibility of economic feasibility.
- Design and manufacture 6-inch PI-2 bundles reaching greater than 400 Nm^3/hr feed at 90% CO_2 recovery and greater than 58% CO_2 purity.
- Field-test 6-inch bundles at 0.3-MWe scale with real flue gas at NCCC.
- Complete a techno-economic analysis (TEA) to evaluate potential to meet greater than 90% carbon capture at a cost of electricity (COE) of 30% less than U.S. Department of Energy (DOE) baseline.

technical content

Air Liquide developed a next-generation membrane material, PI-2, for application with their novel, sub-ambient temperature, membrane-based CO_2 capture technology. The process combines the use of commercial polyimide (PI) hollow-fiber membrane bundles with cryogenic operation to selectively remove the CO_2 from flue gas.

Figure 1 presents a simplified block diagram of the cold membrane process. A highly selective membrane provides pre-concentration of CO_2 prior to CO_2 partial condensation in a liquefaction unit. The membrane is operated at sub-ambient temperature, approximately -30°C, for enhanced CO_2/nitrogen (N_2) selectivity. The cryogenic heat exchanger system provides energy integration between the membrane and the CO_2 liquefaction system.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Sub-Ambient Temperature Membrane

participant:
American Air Liquide Inc.

project number:
FE0026422

predecessor projects:
FE0013163
FE0004278

NETL project manager:
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principal investigator:
Alex Augustin
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alex.augustine@airliquide.com

partners:
Air Liquide Engineering; Air Liquide – ALAS; Parsons Corporation

start date:
10.01.2015

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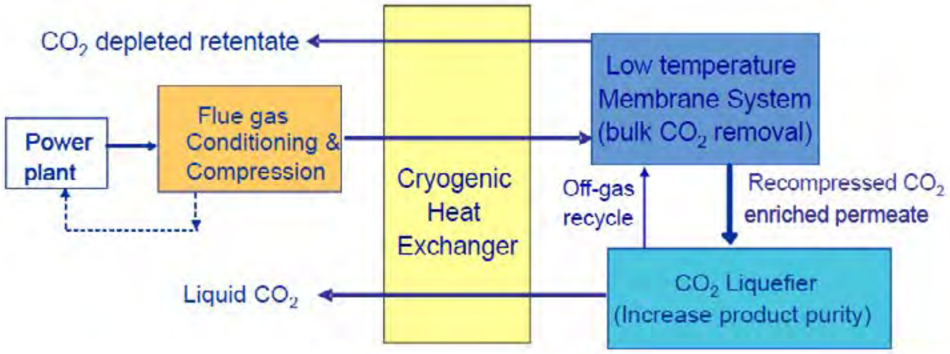

Figure 1: Block diagram of the cold membrane process.

Figure 2 shows a schematic diagram of the hybrid cold membrane process. The process lines in Figure 2 are color-coded (black for ambient temperature, dark blue for approximately -30°C, and light blue for approximately -50°C). The pre-treated flue gas is compressed to approximately 230 pounds per square inch (psi; 16 bar). The heat of compression is captured in boiler feed water, raising its temperature to approximately 147°C. The compressed flue gas is then dried in a dehydration unit to prevent water condensation when the stream is cooled in the brazed aluminum heat exchanger to approximately -40°C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with approximately 1.8% CO_2 at approximately 215 psi (15 bar) and a permeate stream with 60–70% CO_2 at approximately 17 psi (1.1 bar). After the residue is sent through the heat exchanger, further cooling and energy recovery is done via a series of turbo-expanders with the resulting stream at -57°C. The cold stream is again sent through the heat exchanger to provide cold for the overall process. Finally, the excess pressure energy remaining in the warmed residue is partly recovered in a warm turbo-expander before venting. A fraction of the vent gas is used to regenerate the drier. The permeate stream is recompressed, cooled in the heat exchanger, and undergoes phase separation in the cryo-phase separator. Liquid CO_2 is pumped from the separator to provide a storage-ready product CO_2 at approximately 870 psi (60 bar), or greater, and 20°C. The overhead from the cryo-phase separator is warmed through the heat exchanger and then undergoes energy recovery in a turbo-expander. This stream is mixed with the incoming dried flue gas, which raises the mixed feed concentration entering the membrane to 18% CO_2. The higher CO_2 content improves system recovery and efficiency of the membrane separation.

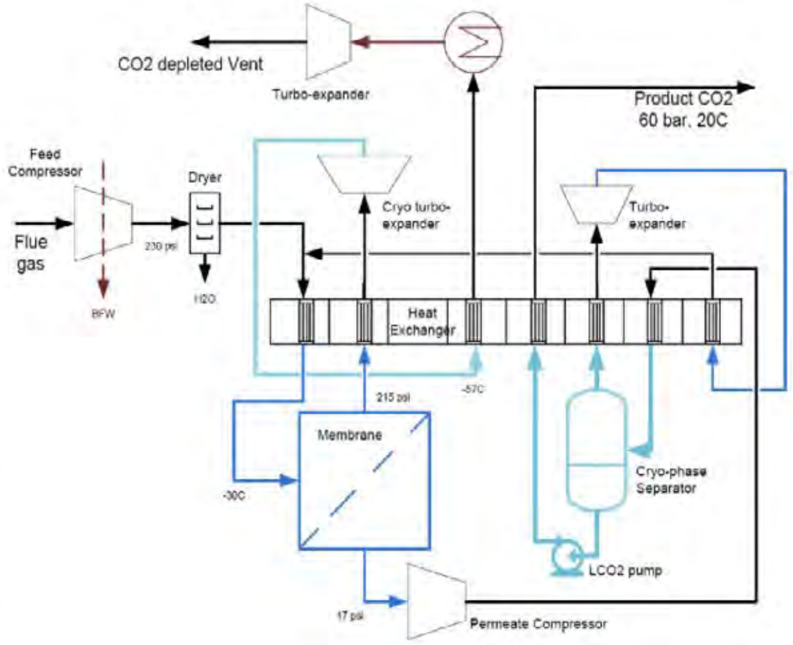

Figure 2: Schematic diagram of cold membrane process.

For most membrane materials, permeability decreases, and selectivity increases with a decrease in operating temperature. However, laboratory measurements of Air Liquide's commercial PI hollow-fiber membranes operated at temperatures below -20°C show two- to four-times higher CO_2/N_2 selectivity with minimal loss of CO_2 permeance compared to ambient temperature values. Closed-loop, bench-scale (0.1 MWe) testing of Air Liquide's existing low-cost commercial membranes (PI-1) was conducted at sub-ambient temperatures in project FE0004278 using synthetic flue gas (CO_2 and N_2). The 6-inch bundles exhibited stable performance over eight months of operation and 12-inch bundles showed excellent mechanical integrity for two months. Preliminary data indicated that 12-inch bundle performance was lower compared to the 6-inch bundles due to non-ideal flow conditions. By modifying bundle fabrication methods and incorporating a membrane sweep stream in the process, productivity of the 12-inch bundles was improved by approximately 30%.

A novel membrane material, PI-2, showed similar high selectivity and greater than five times the fiber permeance of PI-1 in initial laboratory testing with simulated flue gas. PI-2 has the potential for a significant reduction in membrane system cost as productivity increases as the membrane is scaled to 4-inch and 6-inch bundles. Air Liquide's manufacturing methodology was applied to fabricate prototype (4-inch) membrane modules from PI-2 material. Multiple 4-inch prototype PI-2 membrane modules achieved greater than 90 Nm^3/hr productivity at 90% capture and greater than 58% CO_2 purity through testing on the 0.1-MWe bench-scale skid with synthetic flue gas. Once the manufacturing methods proved reliable with the new material, and performance was validated, 6-inch, commercial-scale bundles were fabricated. The new PI-2 material enables further reduction in the cost of CO_2 capture by reducing the number of membrane modules and associated equipment in the system. The PI-2 membranes were tested at 0.1- to 0.3-MWe scale with actual flue gas to validate the membrane performance and allow for a direct comparison with the PI-1 material based on identical test equipment and conditions. The 1-inch PI-2 permeators and PI-1 commercial-scale bundles completed more than 500 hours of steady-state testing on the 0.3-MWe test unit at NCCC, showing stable performance.

A 0.3-MWe field-test unit (Figure 3) was fabricated and installed at NCCC for parametric testing and long-term continuous runs on the optimized PI-1 membrane modules, as well as the advanced high-permeance PI-2 membrane modules. Dynamic tests to quantify the performance of the carbon capture system provided data for a final TEA for a 550-MWe power plant with optimized membrane bundles to assess the system's ability to reach the targets of greater than 90% CO_2 capture and greater than 95% purity at a capture cost approaching $40/tonne.

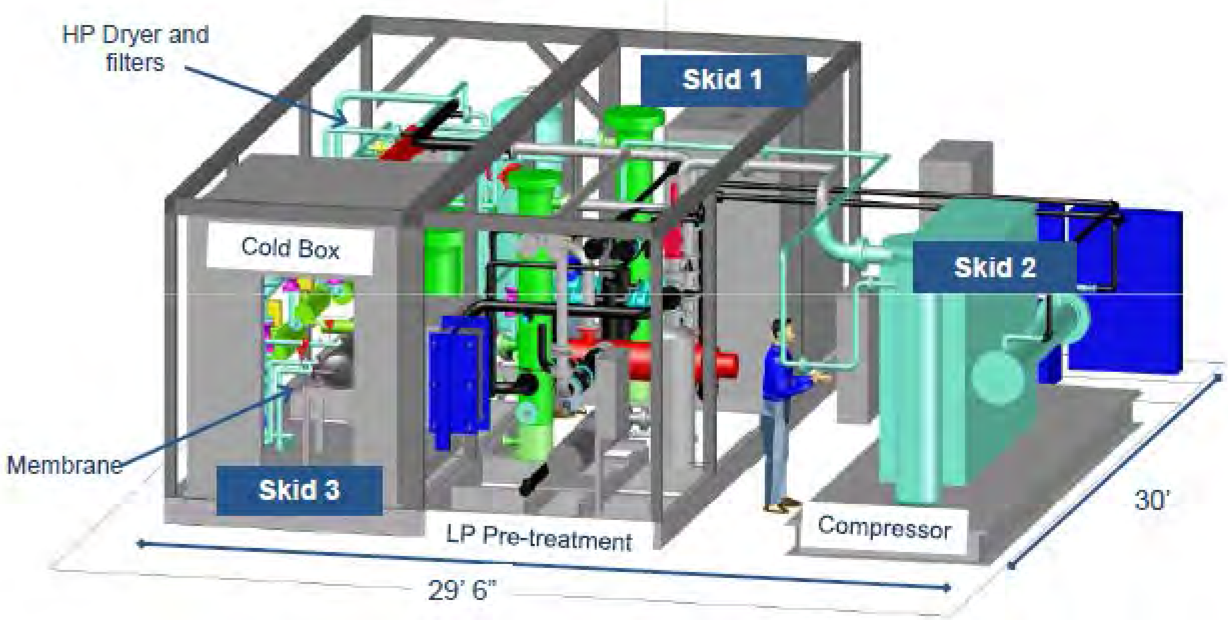

Figure 3: 0.3-MWe test unit at NCCC, Pilot Bay 3.

Multiple 6-inch PI-2 bundles achieved greater than 400 Nm^3/hr productivity at 90% capture and 58% CO_2 purity through testing on the 0.3-MWe field-test unit with real flue gas. As shown in Figure 4, testing at NCCC in 2019 showed stable bundle performance on the 6-inch PI-2 membranes for more than 700 hours. This total period was achieved over two long-term stability test periods (February–March and April–May), with a parametric testing period in between. The parametric testing involved feed temperatures down to -60°C. The bundle performance dropped after being exposed to high CO_2 activity (18% CO_2 at 200 psi and -60°C). Thus, the optimum temperature for PI-2 may be warmer (-30 to -40°C) than the case for PI-1. This distinction may be related either to the greater CO_2 plasticizability of the PI-2 material or the membrane skin morphology differences.

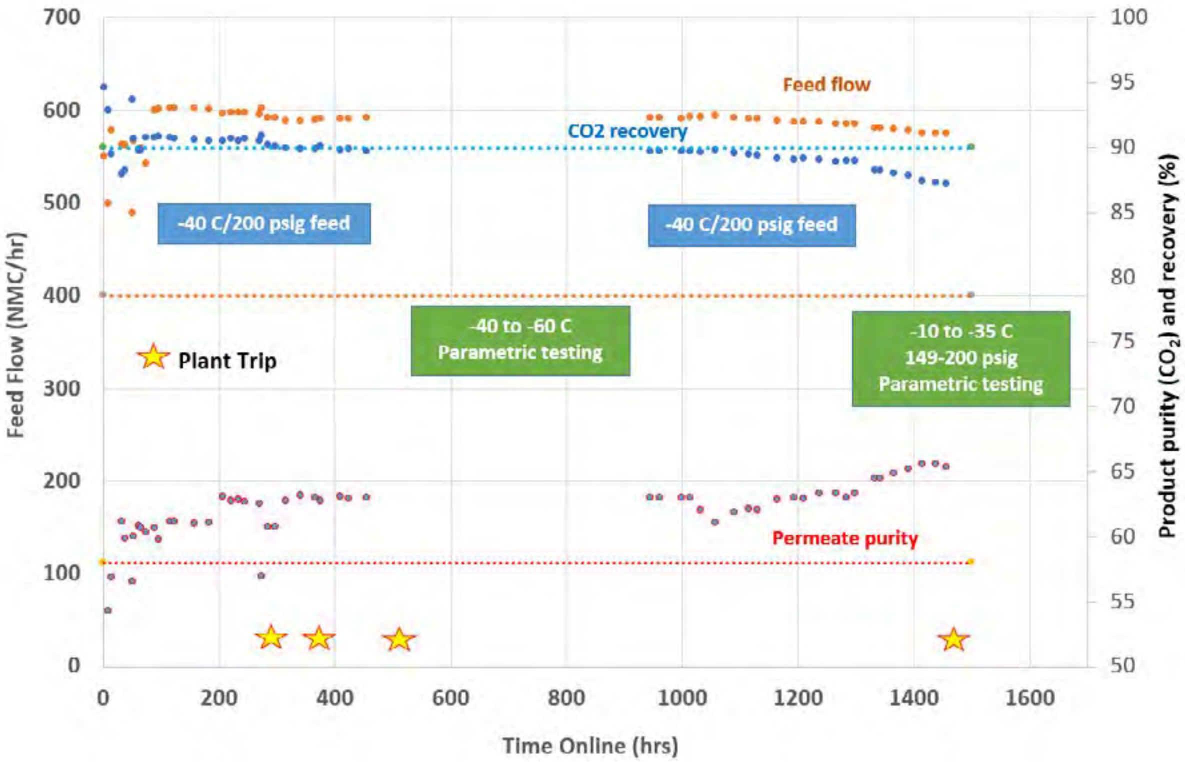

Figure 4: Commercial-scale PI-2 bundle testing data.

Aspen HYSYS was used to model and simulate the cold membrane hybrid process. Two full process models—the standard cold membrane process utilizing the advanced PI-2 membranes and a hybrid process incorporating the use of a gas turbine—were optimized and validated to reduce the overall capture cost and improve the efficiency of the process. Results from the novel hybrid simulation work were combined with measured membrane performance to conduct a TEA for a 550-MWe (net) supercritical pulverized coal (PC) power plant integrated with Air Liquide's hybrid cold membrane carbon capture process. The TEA study includes five cases utilizing the Air Liquide commercial PI-1 membrane bundle and next generation, higher permeance PI-2 membrane, evaluated for CO_2 capture from coal power plant flue gas to produce greater than 99.99 vol.% CO_2 at 2,215 pounds per square inch absolute (psia) pressure. The 12-inch PI-2 membrane was projected to result in a capture cost of approximately $4/tonne CO_2 lower than PI-1 due to reduced membrane cost, resulting in approximately $32/tonne of CO_2 captured. The cold membrane process design and cost estimation have been validated by a third-party, Parsons Government Service.

Hybrid process configurations, such as membrane/absorption or membrane/sorbent processes, have also been proposed incorporating PI-2 membrane material to reduce the compression energy penalty.

The membrane and process parameters identified to date are provided in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polyimide	polyimide
Materials of Fabrication for Support Layer	—	polyimide	polyimide
Nominal Thickness of Selective Layer	µm	<0.1 µm	<0.1 µm
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	20
Hours Tested without Significant Degradation	—	PI-2: 4-inch bundle 340 hrs (synthetic flue gas) PI-2: 6-inch bundle 3,800+ hrs (actual flue gas)	500+ hours (actual flue gas)
Manufacturing Cost for Membrane Material	\$/m^2	-	-
Membrane Performance			
Temperature	°C	-30°C to -45°C	-30°C to -45°C
CO_2 Pressure Normalized Flux	GPU or equivalent	PI-2 6-inch bundle: 657 Nm^3/hr of bundle productivity	400 Nm^3/h
CO_2/H_2O Selectivity	—	<0.2 (dry gas)	<0.2 (dry gas)
CO_2/N_2 Selectivity	—	>50	>70
CO_2/SO_2 Selectivity	—	0.3	0.3
Type of Measurement	—	6” bundle parametric and long-term testing with actual flue gas	6” bundle parametric and long-term testing with actual flue gas
Proposed Module Design		(for equipment developers)	
Flow Arrangement	—	hollow fiber	
Packing Density	m^2/m^3	approximately 1,500 m^2/m^3	
Shell-Side Fluid	—	CO_2-rich permeate	
Flue Gas Flowrate	kg/hr	>400 Nm^3/hr / 6-inch bundle	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80-90%, >95% purity in hybrid process (>58% CO_2 purity from membrane), 16 bar	
Pressure Drops Shell/Tube Side	bar	0.1 bar shell side/1 bar tube side	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	100	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane’s permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units). Bundle productivity in terms of feed flow rate in Nm^3/hr is reported.

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Nominally based on solution-diffusion.

Contaminant Resistance – Expected to be resistant to acidic components based on experience to date.

Flue Gas Pretreatment Requirements – Particulate removal and acid component removal to meet compressor specifications, dehydration to meet cold box specifications, Hg removal to meet heat exchanger specification.

Membrane Replacement Requirements – Membrane productivity decline was too small to be quantified in bench-scale test with synthetic gases.

Waste Streams Generated – Acidic water.

Process Design Concept – See Figure 2.

technology advantages

- Novel high flux PI-2 material enables a significant reduction in membrane area and corresponding capital cost.
- Sub-ambient operation improves membrane performance.
- Process design provides partial recovery of the flue gas compression energy.
- Process design provides an economic method of cooling the flue gas feed to the required sub-ambient temperature for optimal membrane operation without external refrigeration.
- The process design can be combined with a novel scheme for contaminant (sulfur dioxide [SO_2], nitrogen oxide [NO_x]) removal.
- The membrane performance has been validated with greater than 3,000 hours testing with real flue gas at NCCC.

R&D challenges

- Sub-ambient membrane operation requires development of suitable membrane module materials with adequate permeance and selectivity in a commercial membrane module.
- Long-term membrane module performance stability.
- Integration of sub-ambient membrane process, including energy integration with the CPU, as well as energy integration with the power plant, such as compression and turbo-expansion schemes, heat economizers, and energy conservation.
- Flue gas contaminant-specific challenges, including acid gas (SO_2, NO_x) separation, compressor materials of construction, particulate removal, Hg removal, and water management.
- Novel PI-2 material development must achieve tolerance to operating pressure/temperature, effective epoxy seals, long-term stability, and manufacturing reproducibility.
- PI-2 bundle performance deteriorates at colder temperature (less than 45ºC) and higher CO_2 feed concentration.

status

The project was completed in December 2019. The 4-inch and 6-inch PI-2 membrane bundles were successfully fabricated and exceeded the success criteria, with the 4-inch prototype bundles achieving 160 Nm^3/h productivity and 69% CO_2 purity at 90% recovery and the 6-inch achieving 655 Nm^3/hr, and 90% CO_2 recovery at 59+% permeate purity. The 6-inch bundles also completed long-term stability testing with a total of greater than 500 hours of stable data.

available reports/technical papers/presentations

Fu, Shilu, "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/S-Fu-Air%20Liquide-Next-Gen-Hollow-Fiber.pdf*.

Augustine, A., "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/A-Augustine-AAL-Next-Generation-Hollow-Fiber-Modules.pdf*.

Augustine, A., "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)/CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas (FE0013163)," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/A-Augustine-Air-Liquide-Hollow-Fiber-Modules.pdf*.

Augustine, A., "Project Review: Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/A-Augustine-AirLiquide-Hollow-Fiber-Membrane-Modules.pdf*.

Chaubey, T., "CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/T-Chaubey-AirLiquide-Cold-Membrane-Operation.pdf*.

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Hasse, D., et al., "CO_2 Capture by Cold Membrane Operation," presented at the International Conference on Greenhouse Gas Technologies, October 2014.

Chaubey, T., "CO_2 Capture by Cold Membrane Operation with Actual Coal-Fired Power Plant Flue Gas," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/T-Chaubey-AL-CO2-Capture-by-Cold-Membrane-Operation.pdf*.

"CO_2 Capture by Cold Membrane Operation," GHGT-12, Energy Procedia, 2013.

"CO_2 Capture by Subambient Membrane Operation," Final Report, January 2013.

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Sanders, E., "CO_2 Capture by Sub-Ambient Membrane Operation," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

Kulkarni, S.S., et al., “CO_2 Capture by Sub-Ambient Membrane Operation,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.

Solid-Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes

primary project goal

Luna Innovations is pursuing a systems-level approach to demonstrating a dual-phase membrane solid support technology for carbon dioxide (CO_2) separation. Luna is evaluating yttria-stabilized zirconia (YSZ) and its derivatives as standalone solid-phase supports and in the presence of a single molten carbonate electrolyte. Through modification of current YSZ supports, development of structure-property relationships, and prototype modeling of scaled-up technology form factors, Luna's solid-phase supports will have the unique potential to provide the performance and scalability to separate CO_2 from flue gas in the heat recovery steam generators (HRSGs). Successful demonstration of this dual-phase carbon capture and storage (CCS) technology will pave the way for retrofit in high-temperature exhausts found in power plant HRSGs.

technical goals

- Establish performance and design requirements for the dual-phase membrane technology, including the system, safety, and operating parameters for HRSG integration. Expand multitube module test capabilities.
- Design and fabricate a scalable CO_2 separation module prototype.
- Perform relevant testing on single and multitube membrane assemblies. Evaluate performance under relevant conditions in long-term (~months) tests to establish membrane durability and stability.
- Conduct a systems-level analysis and evaluate techno-economic viability.
- Evaluate membrane module performance results and create a module design for pilot-scale testing. Develop Phase III plan.

technical content

Luna Innovations, in partnership with Nooter/Eriksen, is leading the scale-up and demonstration of a new type of dual-phase membrane technology. The dual-phase membrane consists of a thin wall of nanoporous ceramic solid phase that retains a non-volatile molten phase within the pores with capillary action. The molten liquid phase selectively sorbs CO_2 with high concentrations and transport rates. The dual-phase membrane has been advanced with an active transport mechanism that powers CO_2 separation with H_2O's concentration gradient. This results in superior separation performance with an unrivaled combination of CO_2 permeability and selectivity of CO_2 over nitrogen (N_2). This Small Business Innovation Research (SBIR) program is focusing on developing YSZ nanoporous solid-phase materials to achieve the mechanical performance and form factors required for integration and operation inside an HRSG or boiler for operation at 150–500°C.

Currently, there is an unmet need for commercialized membrane systems that can efficiently separate CO_2 from power plant flue gas exhausts at thermally favorable conditions with reduced costs. The proposed solution is to develop an active transport membrane that uses the difference in water vapor concentration between low-pressure steam and the flue gas to drive CO_2 separation through the

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Membrane Support Materials & Module Design

participant:
Luna Innovations

project number:
SC0017124

predecessor projects:
N/A

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partners:
Lawrence Livermore National Laboratory; Nooter/Eriksen; University of Illinois Chicago; Trimeric Corporation

start date:
02.21.2017

percent complete:
85%

membrane. This approach has the potential to lower the total power plant parasitic power costs for carbon capture and compression by 30–40% in comparison with state-of-the-art solvent capture according to full-plant performance modeling in Thermoflex. These high-temperature membranes have greater potential for large-scale, energy-efficient separation by being directly integrated within power plant HRSGs, as shown in Figure 1. Luna's dual-phase membrane technology shows potential for meeting the power generation industry's needs by separating CO_2 from power plant flue gas under operational conditions (150–500°C) and with drastically reduced costs.

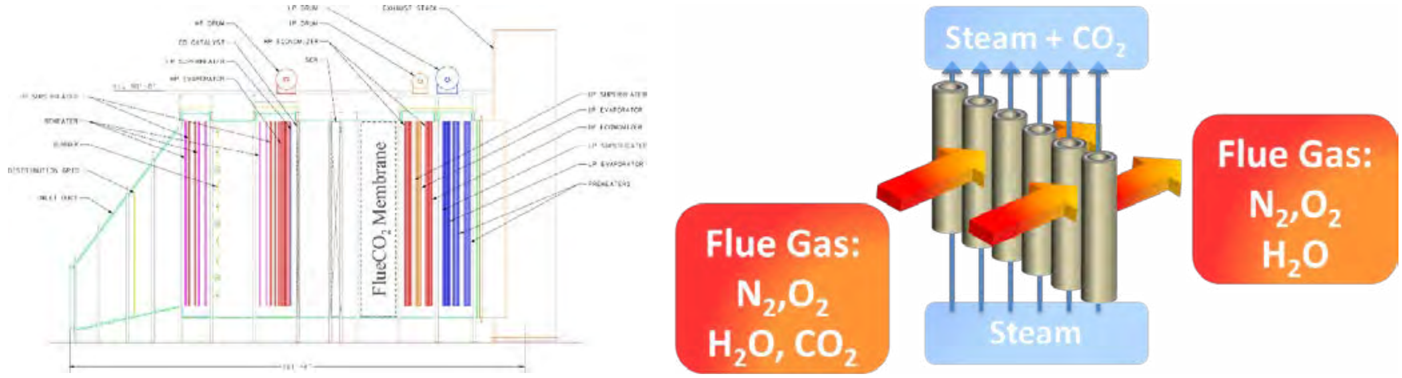

Figure 1: Luna's dual-phase membrane technology introduces a unique ability to implement carbon capture technologies into power plant HRSGs (150–500°C).

In the dual-phase membrane technology, a porous, solid material supports a non-volatile liquid electrolyte. Carbon dioxide actively absorbs into the molten electrolyte at the flue gas side, diffuses through the membrane as the carbonate ion (CO_3^{2-}) from high to low concentration, and desorbs from the membrane into a steam sweep gas (Figure 2). The steam sweep serves to both chemically desorb CO_2 and minimizes the concentration of permeated CO_2.

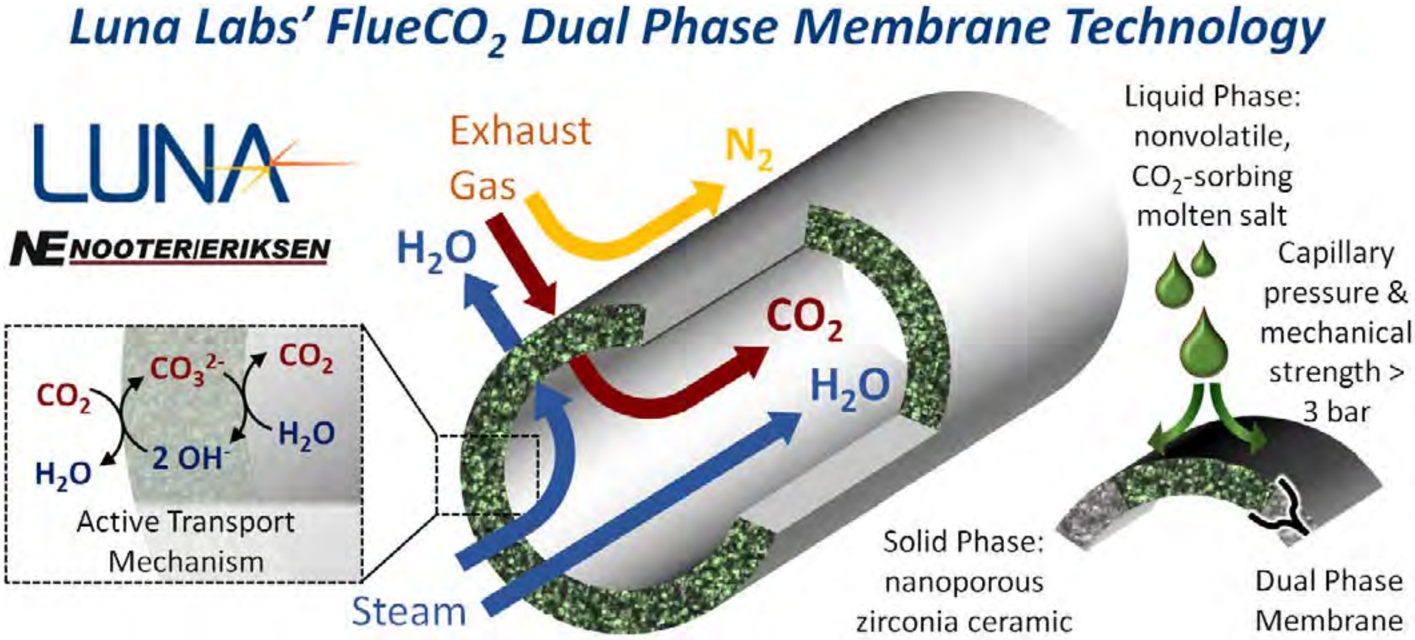

Figure 2: Luna Innovations dual-phase membrane technology for highly efficient and scalable CCS.

The unique operational conditions and performance capabilities of Luna's membrane enables a new opportunity to achieve more energy-efficient and less-expensive carbon capture. This membrane is not limited by the same physics governing Robeson's upper bound as conventional, polymer-based membranes and enables unrivaled combinations of permeability and selectivity (Figure 3). Such a novel system has never before been scaled-up to demonstrate the technical feasibility at the membrane module scale. The operating parameters of the membrane system are shown in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Molten hydroxide dual phase	
Materials of Fabrication for Support Layer	—	Metal oxide	
Nominal Thickness of Selective Layer	µm	950	<50
Membrane Geometry	—	tubes	cartridge
Max Trans-Membrane Pressure	bar	1.3	1.3
Hours Tested without Significant Degradation	—	400	5,000
Manufacturing Cost for Membrane Material	$/m^2	750	1,200
Membrane Performance			
Temperature	°C	150 - 550	150 - 550
CO_2 Pressure Normalized Flux	GPU or equivalent	800	>6,000
CO_2/H_2O Selectivity	—	undetermined	1
CO_2/N_2 Selectivity	—	999	>99
CO_2/SO_2 Selectivity	—	undetermined	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	75	
Shell-Side Fluid	—	steam	
Flue Gas Flowrate	kg/hr	2,200	
CO_2 Recovery, Purity, and Pressure	%/%/bar	98%, >99%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.01/sweep: <0.03	

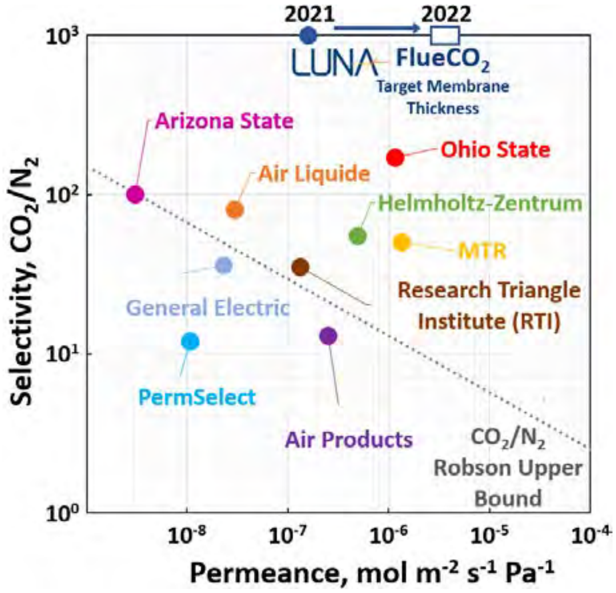

Figure 3: In a Robeson plot comparison, the Luna team's membrane (star) outperforms other CO_2 separation membrane technologies funded by the National Energy Technology Laboratory (NETL).

In Phase I of this project, the Luna Innovations team targeted solid-phase support materials with high strength, increased CO_2 separation capabilities, and stability in the presence of the new molten electrolyte formulations. It was critical that these materials were evaluated in context of the HRSG operational conditions to demonstrate their mechanical, thermal, and chemical stability, as well as their scale-up to larger membrane systems. Luna developed the capability to manufacture membranes using nanoporous YSZ tubes procured from CoorsTek Ceramics. The nanoporous (~100 nm) ceramic materials from CoorsTek are 4 mol% YSZ tubes with 1/4-inch outside diameter (OD) and 3/16-inch inside diameter (ID). These tubes are initially extruded to 120 centimeters (cm) and then cut into smaller segments for this stage of testing by Luna. The mechanical properties of this high-strength ceramic material were characterized and determined to be scalable for the operational conditions expected for the membrane. The solid-phase materials, fabrication methods, and design features were successfully developed in Phase I to manufacture and test multitube membrane modules in Phase II. Media and Process Technology began supplying the ceramic materials in the Phase II project. The methods for manufacturing complete membrane systems from the ceramic materials has been scaled-up to simultaneously manufacture multiple tube membranes using process automation. Quality control procedures have been developed for key stages of the manufacturing process.

Luna has reviewed the options for designing the CO_2 separation membrane module. Tube-based form factor designs remain the most reliable option for further developing and scaling-up the membrane technology primarily based upon the maturity of possible ceramic material manufacturing methods, as well as the supporting technical capabilities required to develop a complete, functional membrane module. The current tube module design is based upon a Swagelok flange and custom interface to multiple short tube samples (Figure 4). This design minimizes module development costs by using commercially available off-the-shelf (COTS) parts whenever possible, while also supporting flexibility and adaptability. The goal is to develop and demonstrate the construction and operation of a small module of six 40-cm long single tubes. Once the basic design and construction approach is established, it is expected to be relatively easy to scale-up by using larger numbers of longer tubes. Larger Swagelok flange sizes will enable scale-up to 19 single-channel tubes or eight of the multichannel tubes. CoorsTek tube lengths can be extended to 120 cm. The initial multitube module has been manufactured and demonstrated to enable scaled-up test and evaluation. A more advanced cartridge membrane design has been developed through multi-physics modeling that includes computational fluid dynamics. Proprietary cartridge membrane features have been developed to simplify manufacturing, increase surface area packing density, and minimize pressure drop while enhancing exhaust gas mixing. Intentional exhaust gas mixing was required because the laminar flow patterns developing at 2.0–2.5 m/s exhaust gas flow rates result in depleted CO_2 concentrations at the membrane surface.

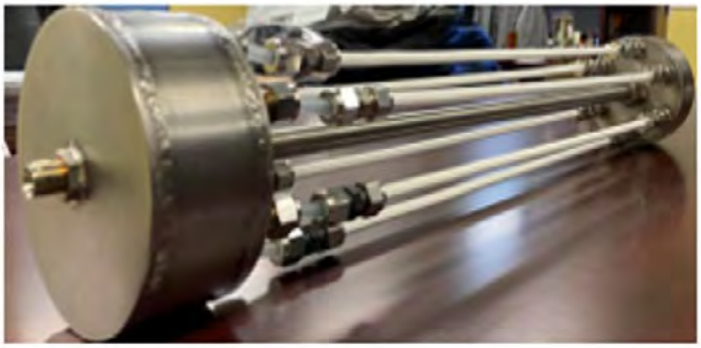

Figure 4: The non-proprietary multitube membrane module with six tubes has been revised to reduce the manufacturing time and costs, while also enabling easier and more flexible modifications for evolution and scale-up.

Luna has continued to achieve both faster CO_2 permeation rates and lower operational temperatures (Figure 5). The transition to lower operational temperatures is important to enable installation of the membrane system into the HRSG near the low-pressure steam evaporator, where the flue gas has reached temperatures 150–200°C. Capturing the CO_2 at lower temperatures lowers separation energy costs. The present low-temperature electrolyte was selected for high CO_2 permeation rates, as well as a relatively wide operational temperature range of 150–300°C. The low-temperature limit of the membrane is generally governed by the freezing of the molten electrolyte phase.

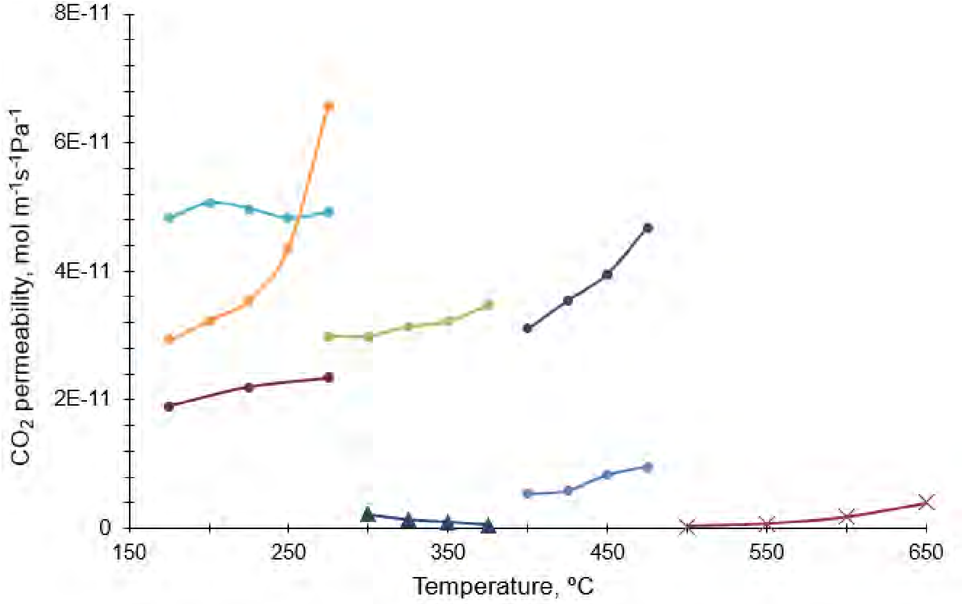

Figure 5: Progress in both improving the CO_2 permeability and decreasing the membrane operational temperatures for more efficient integration into new and retrofitted HRSGs of NGCC power plants.

Nooter/Eriksen has modeled the integration of the CO_2 capture membranes into a natural gas combined cycle (NGCC) power plant (Figure 6). The FlueCO₂ NGCC was derived directly from the National Energy Technology Laboratory (NETL) B31A base case and features a proprietary approach to recovering electrical power. The energy penalty of carbon capture by the FlueCO₂ NGCC are 7% in comparison against the simulated B31A case. The full plant model performances of FlueCO₂ and B31A plants were simulated in Thermoflex as a function of gas turbine load, environmental conditions, and carbon capture rate. Half of the penalty (3.5%) is from the CO_2 compressors and the other half of the energy penalty (3.5%) is due to altered flow of low-pressure steam. The main risk to not achieving this performance target upon scaling-up is in losing the stoichiometric coupling of CO_2 to H_2O by the active transport mechanism (Figure 2). A dynamic cost modeling tool developed to evaluate the membrane unit size as a function of cost predicts a 98% CO_2 capture rate for optimized economics. Nooter/Eriksen has asserted that no features of the FlueCO₂ NGCC plant design will apparently affect the dynamic responsiveness of power output as the plant ramps up/down in load or cycling on/off. Retaining the dynamic flexibility of NGCC power plants is critical for retaining economic competitiveness when the supply and demand of power to the electrical grid cycle on a daily basis.

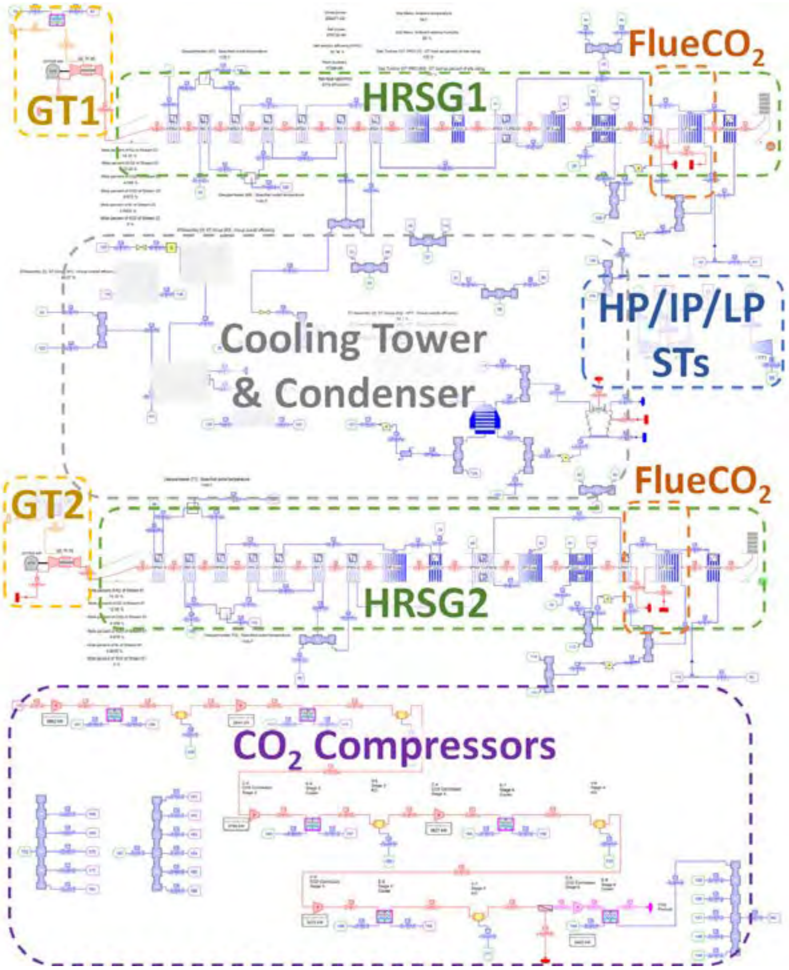

Figure 6: Thermoflex model of $FlueCO_2$ NGCC.

The costing methodology NETL prescribed for the B31A NGCC (base; no carbon capture) and B31B NGCC (control, solvent caron capture) cases were strictly adhered to for economic performance evaluations. Every line of the $FlueCO_2$, B31A, and B31B costing tables were converted into an interactive Microsoft spreadsheet tool that is available upon request for review. The formatting, color coding, and other features of the NETL costing tables have been replicated to facilitate ease of navigation of the spreadsheet costing tool. The spreadsheet costing tool enables direct comparisons between the three NGCC plants for relevant inputs (fuel price, electricity price, capacity factor, 45Q credits, carbon tax, CO_2 capture rate) and outputs (breakeven prices, levelized cost of electricity, 30-year net present value, capital and operating expenses). The $FlueCO_2$ NGCC outperforms the B31B NGCC in plausible scenarios due higher energy efficiency and lower capital costs (Figure 7). The $FlueCO_2$ capital costs of capture are dominated by the membranes and CO_2 compressors. The main risk is failing to achieve the target membrane costs within a five-year lifetime (all other additional equipment is commercially available with established costs). The high capital costs of the B31B plant are compounded by taxes, insurance, and interest. A techno-economic analysis (TEA) was performed as a part of this study. The economic data obtained from the systems-level analysis is shown in Table 2.

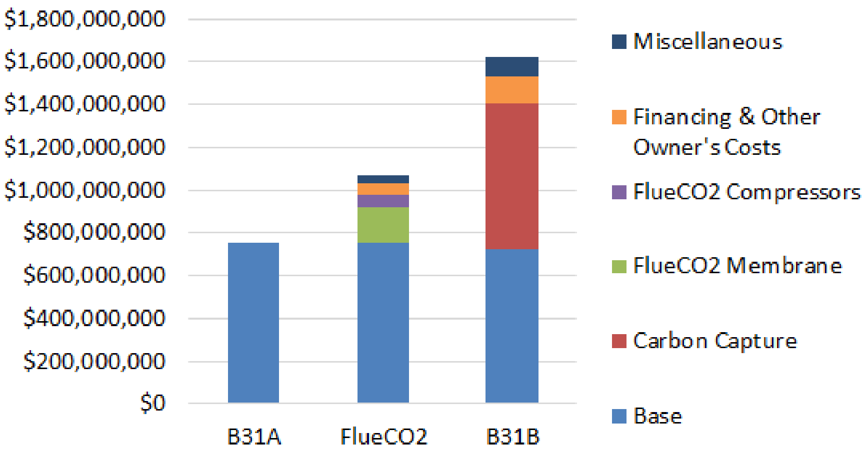

Figure 7: Total as-spent cost (TASC) contributions to the 30-year net present value (NPV) analyses, where B31A = 760 MWe.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Reference (B31B)	Reference (B31A)	Current R&D Value	Target R&D Value
Total As-Spent Cost	$/MW	2,635	1,040	1,713	1,800
Heat Rate	BTU/kWhr	7,159	6,363	7,078	7,100
Cost of Carbon Captured	$/tonne CO_2	69.16	N/A	29.69	35
Cost of Carbon Avoided	$/tonne CO_2	90.48	N/A	42.59	45
Breakeven CO_2 Price	$/tonne CO_2	79.60	N/A	38.18	40
Capital Expenditures	$/MWhr	25.03	9.88	16.12	18
Operating Expenditures	$/MWhr	14.22	5.31	9.82	10
Cost of Electricity	$/MWhr	39.25	15.19	25.93	28
Levelized Cost of Electricity	$/MWhr	70.89	43.31	57.13	60

The approach to retrofitting existing NGCCs is presently under consideration. If the target membrane performance metrics are achieved, there is enough space already available in the HRSG to incorporate the membrane system. The membranes could therefore be incorporated to retrofit existing HRSGs for carbon capture. Retrofits of HRSGs of existing NGCC power plants are expected to comprise the largest and most valuable market to target for commercialization.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the membrane occurs by the high concentration of H_2O in the steam sweep, selective gas sorption reactions (bicarbonate and carbonate mechanisms).

Contaminant Resistance – Significant quantities of ash in coal power plants represents a contaminant hazard for the membranes. NGCC power plants have therefore been identified as the target application.

Flue Gas Pretreatment Requirements – The temperature must be less than 450°C.

Membrane Replacement Requirements – The membrane lifetime is currently unknown.

Waste Streams Generated – The membrane process will generate a zirconia-based composite that may be recyclable.

technology advantages

- High performance separation with active transport mechanism.
- Highly efficient NGCC/HRSG integration approach.
- Low capital and operational costs.
- Modular design allows for easy integration with new and existing power plants.

R&D challenges

- Long-term stability of ceramic materials.
- Retaining membrane cost projections throughout the scale-up process.
- Avoiding steam leakage by active transport mechanism.

status

Phase I of the project was completed in 2017. Phase II objectives (pilot-scale testing, integration with HRSG, system-level analysis) are underway, and a final report is expected by the end of 2022.

available reports/technical papers/presentations

Ceron, M., Lai, L., Amiri, A., Monte, M., Katta, S., Kelly, J., Worsley, M., Merrill, M., Kim, S., Campbell, P. “Surpassing the conventional limitations of CO_2 separation membranes with hydroxide/ceramic dual-phase membranes,” Journal of Membrane Science, 2018, Vol. 567, pages 191-198. *https://www.sciencedirect.com/science/article/pii/S0376738818318209*.

Merrill, M. “Passive CO_2 Separation Membranes for Hot Flue Gases,” presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-Separation-Membranes_Aug%202018.pdf*.

Merrill, M. “Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes,” Phase I Final Review Meeting, Pittsburgh, PA, November 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/DE-SC0017142%20Solid%20Membrane%20Materials%20Final%20Review%20NETL%2020171129.pdf*.

Merrill, M. “Passive CO_2 Separation Membranes for Hot Flue Gases,” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-CO2Separation_Aug%202017.pdf*.

A Process with Decoupled Absorber Kinetics and Solvent Regeneration Through Membrane Dewatering and In-Column Heat Transfer

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER) teamed with Media and Process Technology, Inc. and Lawrence Livermore National Laboratory (LLNL) (through support project FWP-FEW0242) to develop an intensified, innovative carbon dioxide (CO_2) capture process. The project goals were to increase system efficiency and enable significant reductions in capital and operating costs of solvent-based post-combustion capture through: (1) the use of 3D-printed, two-channel structured packing material to control absorber temperature profile and increase the CO_2 absorption rate, thereby allowing decreases in absorber size; (2) implementation of a zeolite membrane dewatering unit capable of substantial dewatering of carbon-rich solvent to decouple solvent concentrations that are optimum for CO_2 absorption and desorption; and (3) utilization of a two-phase flow heat exchanger prior to the stripper, providing a secondary point of vapor generation for CO_2 stripping resulting in significant energy savings.

technical goals

- Design and fabricate an advanced structured packing and a dewatering membrane module.
- Retrofit and test the intensified process on UK CAER's small and large (0.1-megawatt-thermal [MWth]) bench-scale post-combustion CO_2 capture facilities with simulated and coal-derived flue gas.
- Perform a techno-economic analysis (TEA); an environmental, health, and safety (EH&S) risk assessment; and a technology gap analysis.
- Enable reduction of absorber size (compared to baseline conventional absorber) by up to 50% through application of the in situ heat removal structured packing material.
- Attain at least 15% dewatering of the carbon-rich solvent in the process loop.
- Attain 30% energy savings in the solvent reboiler-specific energy consumption.
- Demonstrate the process at 0.1-MWth bench-scale on coal-derived flue gas.
- Collect data to perform the detailed TEA of CO_2 capture process integration to a full-scale, coal-fired power plant.
- Advance this technology to meet U.S. Department of Energy (DOE) capture goals of 95% CO_2 purity at a cost of approximately $30 per tonne of CO_2 captured.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Integrated Advanced Solvent Process for Coal Flue Gas

participant:

University of Kentucky Center for Applied Energy Research (UK CAER)

project number:

FE0031604

NETL project manager:

David Lang
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University of Kentucky
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partners:

Media and Process Technology Inc.; Lawrence Livermore National Laboratory (LLNL); Smith Management Group; Trimeric Corporation

start date:

05.01.2018

percent complete:

100%

technical content

UK CAER's starting point for development of this technology was consideration of the drivers for capital and operating costs of aqueous post-combustion capture process systems. While still utilizing the general process arrangement of CO_2 absorption-desorption by contacting the flue gas with solvent (which might even be a commonly used aqueous solvent such as an amine) in the absorber and water vapor stripping the rich solvent in the regenerator, UK CAER has postulated that significant efficiency and cost savings could be obtained by deploying several reactor improvements in this process and innovations in certain units. The basic process arrangement and units involved are depicted in Figure 1.

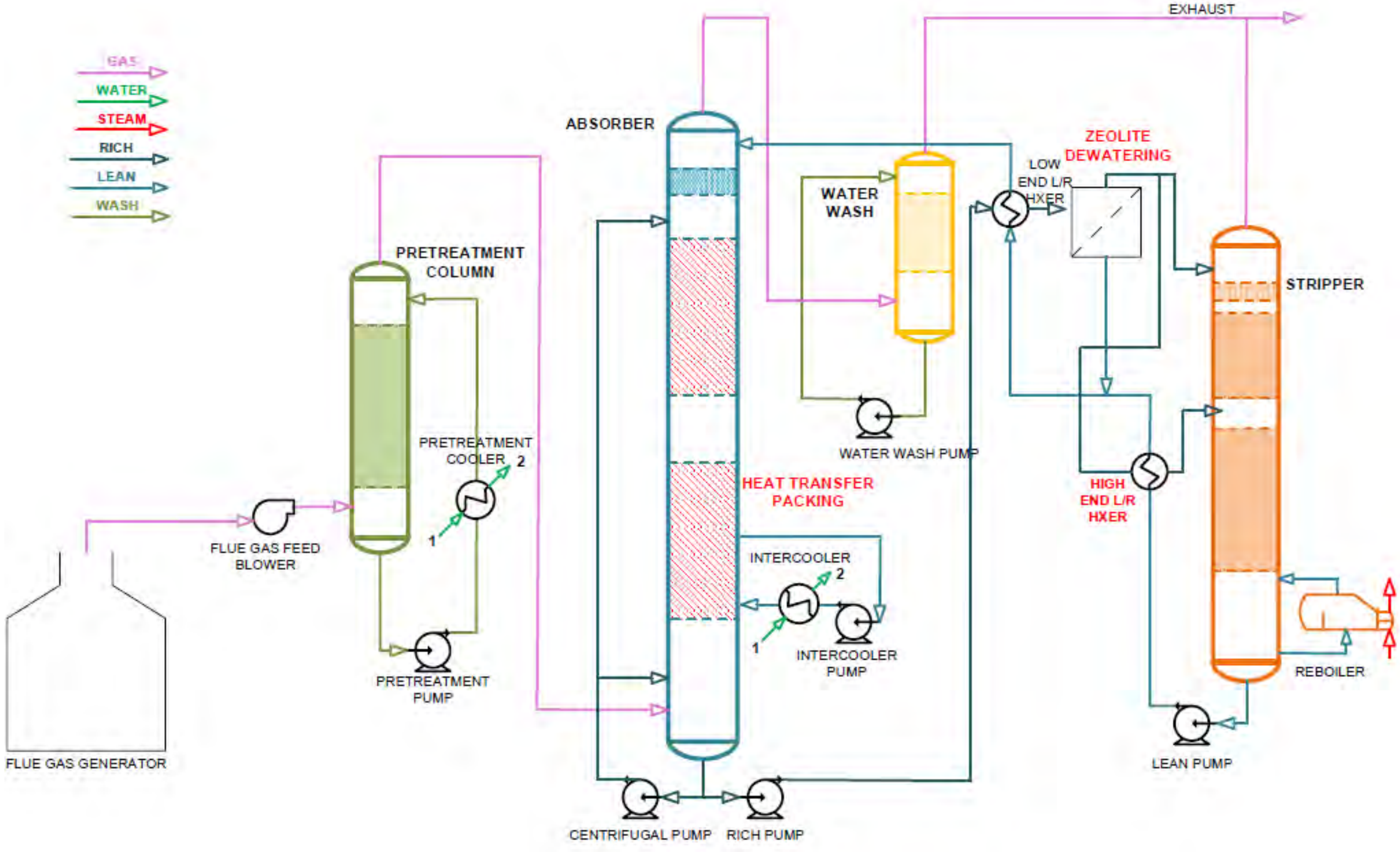


Figure 1: UK CAER CO_2 capture process.

Improvement of Temperature Profile in the Absorber—3D-Printed Packing

The absorber for contacting flue gas with solvent to remove the CO_2 from the flue gas was a packed column type containing either random or structured packing to increase mixing/contacting of the gas and liquid solvent. The diameter of the absorption column was determined by the flooding point at the liquid/gas (L/G) ratio; the diameter must be large enough to prevent flooding. The highest flooding potential for a fast-reacting solvent occurred at a characteristic temperature bulge, which typically occurs in the top packing section, 15–30% of packing height from the top. A measured temperature profile for UK CAER's 0.7-megawatt-electric (MWe) small pilot-scale absorber is shown in Figure 2 for contacting flue gas with amine solvent. With L/G of approximately 3.2, a temperature rise of approximately 50°F is observed about 10 feet below the lean amine feed.

Because the driving force for CO_2 absorption is inhibited by high temperature, temperature excursions like this decrease performance, which means that larger internal column diameter and increased column height (translating directly into increased column cost) would be necessary to accomplish a given required amount of CO_2 capture. However, if internal temperatures in the column can be aggressively managed, column size can be substantially reduced.

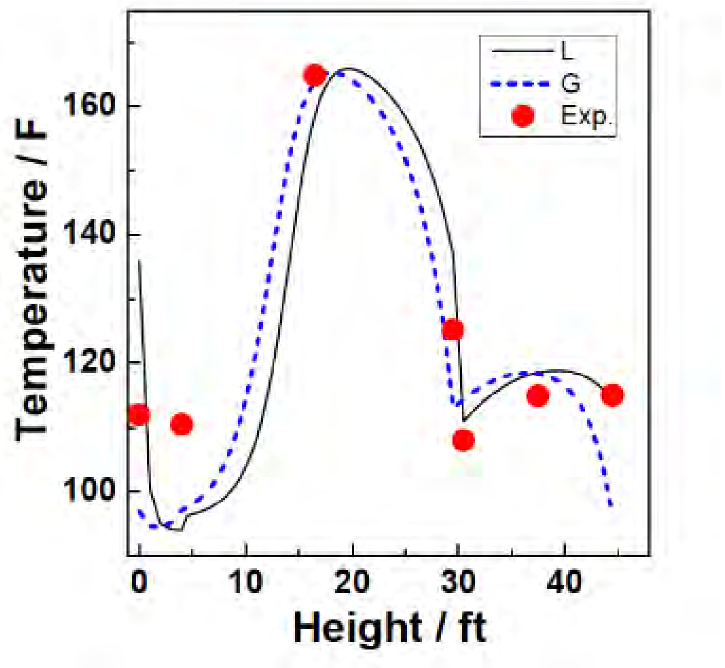


Figure 2: Absorber temperature profile (solid lines indicate model predictions for liquid and gas, experimental data in dots).

The UK CAER team's approach for temperature management in the absorber was to deploy innovative, 3D-printed structured packing that incorporates heat transfer channels in the packing. This provided in-process cooling at appropriate locations without the need for separate, multiple external inter-stage cooling sections (reducing column height). Use of 3D printing/additive manufacturing provided the capability to fabricate the packing with the complex dimensional patterns required at reasonable cost.

Polymeric materials, such as acrylonitrile butadiene styrene (ABS), polystyrene, and high-density polyethylene, were investigated for use. They are stable in the presence of loaded amine solvent at operating temperature, while they are readily amenable to 3D printing via methods such as fused deposition modeling and stereolithography. Figure 3 shows the design (left) and a fabricated unit printed in ABS via stereolithography (middle). Instances of leakage, structural integrity issues, and fouling have occurred with certain polymeric materials made by certain methods; recently, use of direct metal laser sintering to fabricate packing from 316 stainless steel (Figure 3, right) has delivered promising results.

Figure 3: 3D-printed packing.

Evaluation of the performance of the packing for improving the temperature profile in the absorber column has been ongoing using the bench-scale unit at UK CAER. Figure 4 shows results of putting the heat transferred packing material into the column. The solid line is the baseline without the heat transfer packing, and the dotted and dashed lines are with the heat transfer packing in place. Thermocouples were located at regular intervals from position 1 at the top of the column (lean solvent inlet) to position 7 at the bottom (flue gas inlet). Note that the typical temperature increase at positions 2 and 3 in the baseline has been greatly improved when the heat transfer packing is deployed.

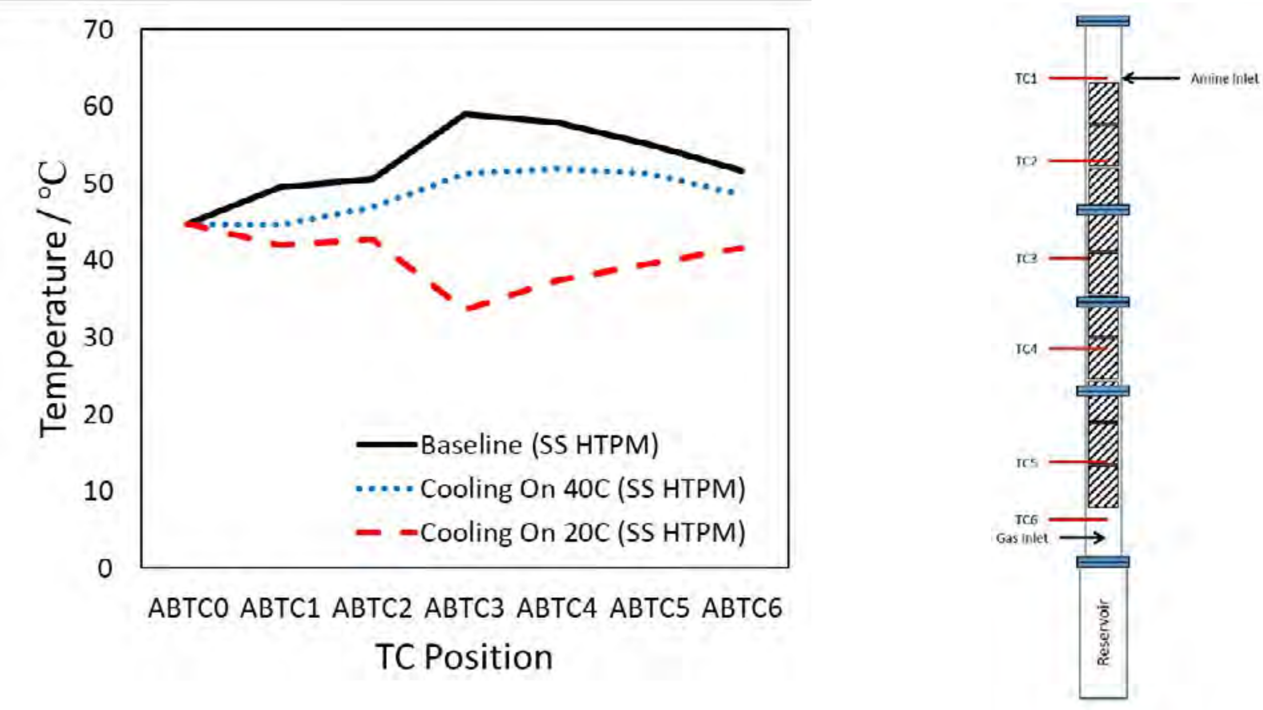


Figure 4: Heat transfer packing effect on absorber column temperature profile.

Dewatering Rich Solvent—Membrane-Based Dewatering Unit

Another element of this innovative process approach was tackling the conflicting requirements for solvent concentrations between the absorber and stripper. In terms of transport phenomena, it is well accepted that the stripper is equilibrium-controlled while the absorber is mass transfer/diffusion-controlled. For the equilibrium-controlled stripper, the carbon loading via CO_2 partial pressure will determine the size of the stripper as well as the energy associated with stripping gases, which typically accounts for approximately 40% of the overall energy required for solvent regeneration. Higher solvent concentrations typically produce higher carbon loadings per kilogram solution at a given temperature compared to a diluted solvent, so more concentrated solvents are preferable for stripper applications. However, higher solvent concentrations always correspond to higher viscosities. For a diffusion-controlled absorber using any advanced fast solvent, the mass transfer coefficient was dominated by the resistance from the chemical reaction of CO_2 and amine in the reaction film and diffusion of unreacted amine and carbamate between the reaction interface and bulk solvent. Unfortunately, the diffusivity between the reaction interface and the bulk solvent was governed by a mildly exponential relationship in which higher solvent viscosity increases the diffusion resistance, thereby reducing mass transfer.

To better attain desired solvent concentrations between the absorber and stripper, a dewatering unit using zeolite membranes was developed and evaluated. The unit receives rich solvent from the absorber and permeates it through membranes, resulting in concentrated solvent retentate and a permeate stream of mostly water. The target was to accomplish at least 15% dewatering of the solvent coming from the absorber in this membrane-based dewatering unit. The permeate water was returned to the absorber after heat recovery, leaving a carbon- and solvent-concentrated solution to enter the stripper for regeneration. This has the dual desired result of lowering energy consumption in the stripper, while simultaneously maintaining more dilute solvent in the absorber so as not to negatively impact CO_2 absorption rates there. The dewatering step is indicated in Figure 1 as Zeolite Dewatering; note that the recovered water is mixed with the lean solvent from the stripper and the combined stream goes to the top of the absorber.

Design and fabrication of the zeolite membrane dewatering modules is an important aspect of technology development. The membranes themselves consist of a thin zeolite layer on a sublayer of dense alumina, all of which is supported on tubes of highly porous conventional alumina. The very dense alumina layer is needed to confine the molecular seed particles to the surface of the alumina, from which the zeolite layer is grown. Figure 5 shows a scanning electron microscopy (SEM) cross-section of a membrane displaying the juxtaposition of these layers, with a fully formed 3.5-µm layer of zeolite on the outside. The membrane tubes are to be deployed in bundles in modules, per the design depicted in Figure 6 for the intended bench-scale testing. Membrane packing density can reach approximately 322 m^2/m^3 in these modules.

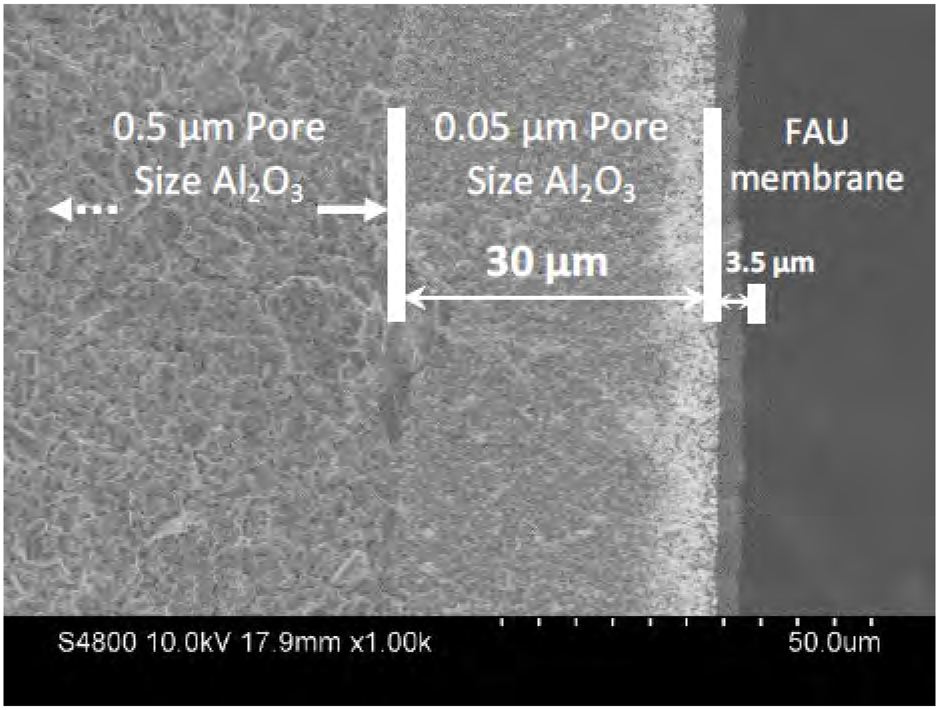
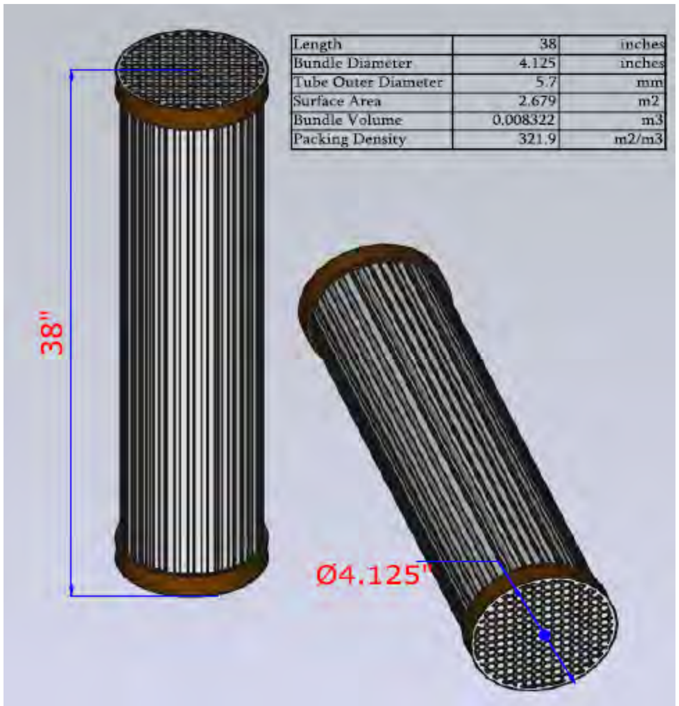


Figure 5: Dewatering membrane structure.



Length	38	inches
Bundle Diameter	4.125	inches
Tube Outer Diameter	5.7	mm
Surface Area	2.679	m2
Bundle Volume	0.008322	m3
Packing Density	321.9	m2/m3

Figure 6: Dewatering membrane module design.

Advanced Stripping and Secondary Vapor Generation Point

An additional improvement in this process approach targets reduction of steam consumption by considerations of phase transitions occurring in the stripper and optimization of heat exchange and points of solvent feed to the stripper. In a conventional stripping process, the stripper reboiler uses extracted steam to evaporate water in the solvent, both as a carrier gas to strip CO_2 out of the solvent and as an energy carrier to heat the stripper to a desired temperature profile as required by the solvent and stripper operating pressure. During this process, significant energy is lost. Secondarily, high rich solvent temperature from the rich/lean heat exchanger entering the stripper prevents the gaseous phase from condensing at the top of the stripper, reducing heat recovery within the system as more water vapor is lost with the gaseous exhaust. Consequentially, the typical temperature profile (left) and CO_2 and water fluxes (right) as a function of height in the stripper have been observed on UK CAER's 0.7-MWe post-combustion capture facility and modeled as plotted in Figure 7. This clearly indicates that most of the CO_2 was liberated from the solvent in the bottom 14 feet or so of the 30-foot-long stripper (corresponding with the nearly flat plateau seen in the right-side panel).

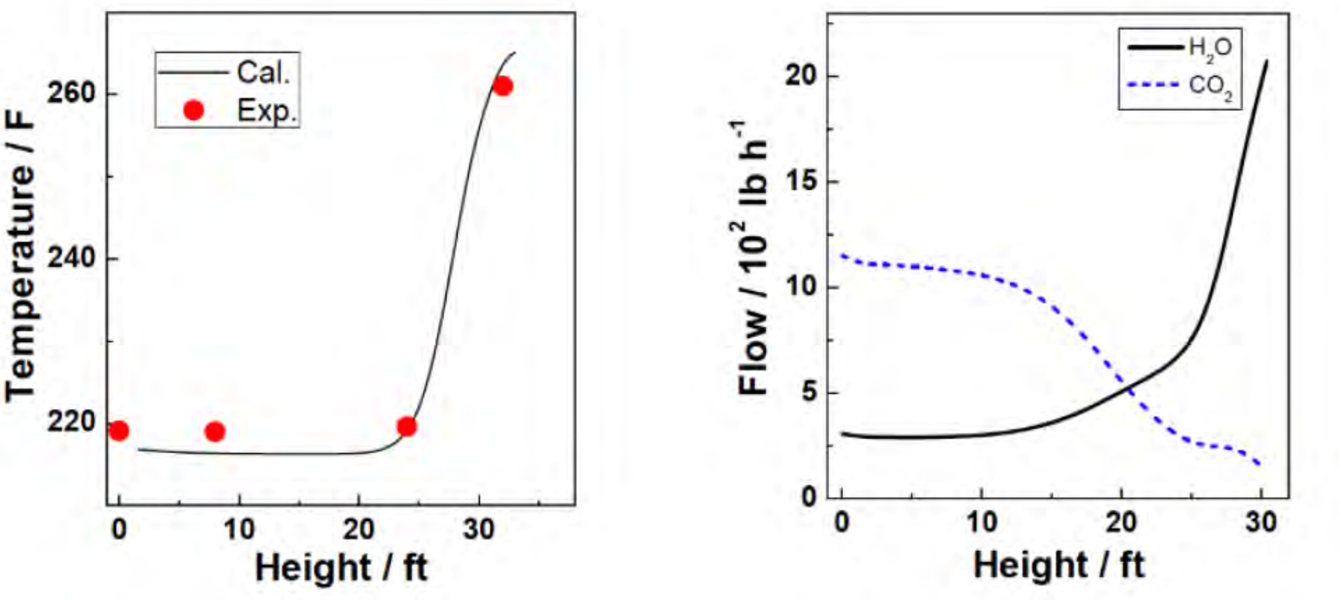


Figure 7: Temperatures and mass fluxes in solvent stripper.

To overcome these inefficient characteristics of the conventional stripper regenerator, UK CAER evaluated a reactor configuration using a secondary entry point for rich solvent feed. The multi-point rich solvent feed was accomplished by dividing the traditional lean/rich (L/R) heat exchanger into two sections—a low-end L/R exchanger and a high-end L/R exchanger (which essentially creates a second source for vapor generation). The basic arrangement of these is diagrammed in Figure 1. The feed to the stripper from the dewatering unit was split into two streams: (1) after the low-end exchanger, about half of the total rich flow with a temperature (solvent and carbon-loading dependent) is fed to the top of stripper packing as a heat sink to condense water vapor and subsequently reduce the water (H_2O)/CO_2 ratio; and (2) the remaining rich flow is heated through the high-end exchanger so that two-phase flow is achieved with 4–6% vapor (solvent and carbon-loading dependent) entering the middle of the stripper packing. This vapor will act as a secondary source of carrier gas for CO_2 stripping. UK CAER modeling indicates the H_2O/CO_2 ratio in the stripper exhaust was significantly reduced from 0.8–1.0 as experienced conventionally, to 0.3–0.4, allowing an approximately 26% reduction in steam consumption.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Zeolite Y	
Materials of Fabrication for Support Layer	—	(if applicable)	
Nominal Thickness of Selective Layer	µm	3.5	5
Membrane Geometry	—	cylindrical	
Max Trans-Membrane Pressure	bar	5	7
Hours Tested without Significant Degradation	—	50	>1000
Manufacturing Cost for Membrane Material	$\$/m^2$	>500	250
Membrane Performance			
Temperature	°C	130	115
CO_2 Pressure Normalized Flux	kg/m^2-h	10	15
Permeate Rejection Rate	—	95%	80%
CO_2/N_2 Selectivity	—	Not applicable	
CO_2/SO_2 Selectivity	—		
Type of Measurement	—	Flux and Carbon Loading in the Liquid	
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Counter-current Flow	
Packing Density	m^2/m^3	400	
Shell-Side Fluid	—	Feed (rich solvent)	
Liquid Flowrate	kg/hr	150	
CO_2 Recovery, Purity, and Pressure	%/%/bar	Not Applicable	
Pressure Drops Shell/Tube Side	bar	<0.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	Not Available	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	34.97	30
Cost of Carbon Avoided	\$/tonne CO_2	57.5	—
Capital Expenditures	\$/MWhr	43.1	40
Operating Expenditures	\$/MWhr	28.3	—
Levelized Cost of Electricity	\$/MWhr	94.8	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The design basis for the TEA was done following guidelines established for DOE/National Energy Technology Laboratory (NETL) Baseline Report, Rev 4, from which Case B12B was compared with the UK CAER CCS technology on a 650-MWe net plant scale.

Scale of Validation of Technology Used in TEA – UK CAER CCS technology was modeled in Aspen Plus on a 650-MWe plant with material and heat balance data used as inputs for the TEA.

Qualifying Information or Assumptions – Operating expenditure reported is the sum of the fixed and variable operating costs. The reported levelized cost of electricity excludes (transportation, storage, and monitoring).

technology advantages

- Reduction in absorber column size, reducing both capital and operating costs.
- Reduction in stripper column size and steam demand for solvent regeneration, reducing both capital and operating costs.
- Applicability to a variety of solvents in absorption-based capture process implementation.

R&D challenges

- Innovative absorber packing fabrication cost, structural/performance integrity, fouling.
- Dewatering membrane unit zeolite membrane fabrication, module integrity.
- Increased controls and control schemes, mainly because of more complicated process flows and heat exchange around the dewatering unit.

status

Absorber testing with deployment of 3D-printed packing material resulted in 10°C temperature reductions, confirming the design concept of structured packing enabling column size reductions. The zeolite membrane-based dewatering has been validated on amine solvent at 10 kg/m^2/hr, and modules with required membrane packing density have been developed. Secondary vapor generation from split rich stream to stripper effectively lowered water vaporization and reduced solvent regeneration energy by at least 15%. Dewatering with zeolite membrane is not cost-effective due to low flux and chemical instability in large quantity fabrication. The UK CAER process improvements provide capital expenditure (CAPEX) reduction, which contribute to a lower cost of CO_2 capture, as well as lowering the parasitic energy demand, resulting in 23% reduction in CO_2 capture cost compared to the reference case B12B.

available reports/technical papers/presentations

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," Project kickoff meeting presentation, May 18, 2018 *http://www.netl.doe.gov/projects/plp-download.aspx?id=10495&filename=A+Process+with+Decoupled+Absorber+Kinetics+and+Solvent+Regeneration+through+Membrane+Dewatering+and+In-Column+Heat+Transfer.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018 *https://netl.doe.gov/sites/default/files/netl-file/J-Landon-UK-Decoupling-Absorber-Kinetics-and-Solvent-Regeneration.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL CCUS Integrated Project Review Meeting, Pittsburgh, PA, August 2019 *https://netl.doe.gov/sites/default/files/netl-file/J-Landon-UoK-Membrane-Dewatering.pdf*.

James Landon, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, BP1 project review meeting presentation, Pittsburgh, PA, October 2019 *http://www.netl.doe.gov/projects/plp-download.aspx?id=10494&filename=A+Process+with+Decoupled+Absorber+Kinetics+and+Solvent+Regeneration+through+Membrane+Dewatering+and+In-Column+Heat+Transfer.pdf*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020 *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Liu.pdf*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021 *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Liu.pdf*.

Kunlei Liu, "*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," University of Kentucky, Final Project Briefing, Pittsburgh, PA, February 2022 *http://www.netl.doe.gov/projects/plp-download.aspx?id=12846&filename=A+Process+with+Decoupled+Absorber+Kinetics+and+Solvent+Regeneration+through+Membrane+Dewatering+and+In-Column+Heat+Transfer.pdf*.

Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost-Effective Carbon Capture

primary project goal

Membrane Technology and Research, Inc. (MTR) is developing composite membranes with superior carbon capture performance using a novel transformational approach. Two membrane targets have been identified: (1) carbon dioxide (CO_2) permeance of 4,000 gas permeation units (GPU) with mixed-gas CO_2/nitrogen (N_2) selectivity of 25, and (2) CO_2 permeance of 3,000 GPU with mixed-gas selectivity of 50. The first type will be used in the CO_2 removal step and the second type will be used in the CO_2 sweep step, both of which are parts of MTR's innovative post-combustion CO_2 capture process.

technical goals

- Develop methods to produce isoporous supports, first manufacturing single-layer supports (14 inches wide) using the laboratory's continuous casting system and then manufacturing dual-layer supports (40 inches wide) using MTR's commercial-scale casting equipment.
- Synthesize and characterize polymers containing high ether-oxygen content for CO_2/N_2 separation, and down-select polymers with most promising CO_2/N_2 separation properties for scale-up and production of composite membranes.
- Prepare composite membranes by coating selective layers onto isoporous support, first using a laboratory-scale coating machine (12 inches wide) and then using MTR's commercial-scale coater (40 inches wide).
- Fabricate and test laboratory-scale spiral-wound and plate-and-frame modules, optimize the design to minimize pressure drop and produce prototype modules of both types for testing at the National Carbon Capture Center (NCCC).
- Design a bench-scale test skid for testing prototype membrane modules.
- Install and operate a test skid at NCCC for at least three months with actual coal-fired flue gas.
- Perform a techno-economic analysis (TEA) and sensitivity analysis of the process.

technical content

MTR is developing composite membranes with superior CO_2 capture performance using a novel transformational approach. Composite membranes consist of a selective polymer layer coated on a support that, ideally, does not hinder transport in the selective layer. MTR has conclusively demonstrated that this objective is not met for current supports when coated with very thin selective layers, leading to a reduction in permeance by a factor of two or larger. The proposed three-year project consists of two parallel technology developments that address the support issue, as well as the development of more selective materials.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Polymeric Membranes with Isoporous Supports

participant:

Membrane Technology and Research, Inc.

project number:

FE0031596

predecessor projects:

N/A

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partners:

State University of New York at Buffalo; University of Texas at Austin

start date:

06.01.2018

percent complete:

60%

The first development is replacing the conventional porous supports used to fabricate composite membranes with novel isoporous supports. The remarkable pore structure of isoporous supports is created through self-assembly of block copolymers and is the ideal surface to support the nonporous layers that perform the separation in composite membranes. Work at MTR has shown that the surface pore structure of conventional supports restricts diffusion in the adjacent selective layers, and this geometrical effect significantly reduces the permeance of layers thinner than 1 micron. The high surface porosity and uniformity in pore size and pore location of the isoporous supports (Figure 1) eliminates this restriction and allows fabrication of Polaris™ composite membranes with significantly increased CO_2 permeances as high as 4,000 GPU. Building on extensive work on isoporous membranes reported in the open literature, the isoporous support preparation methods will be adapted to MTR's commercial membrane casting equipment.

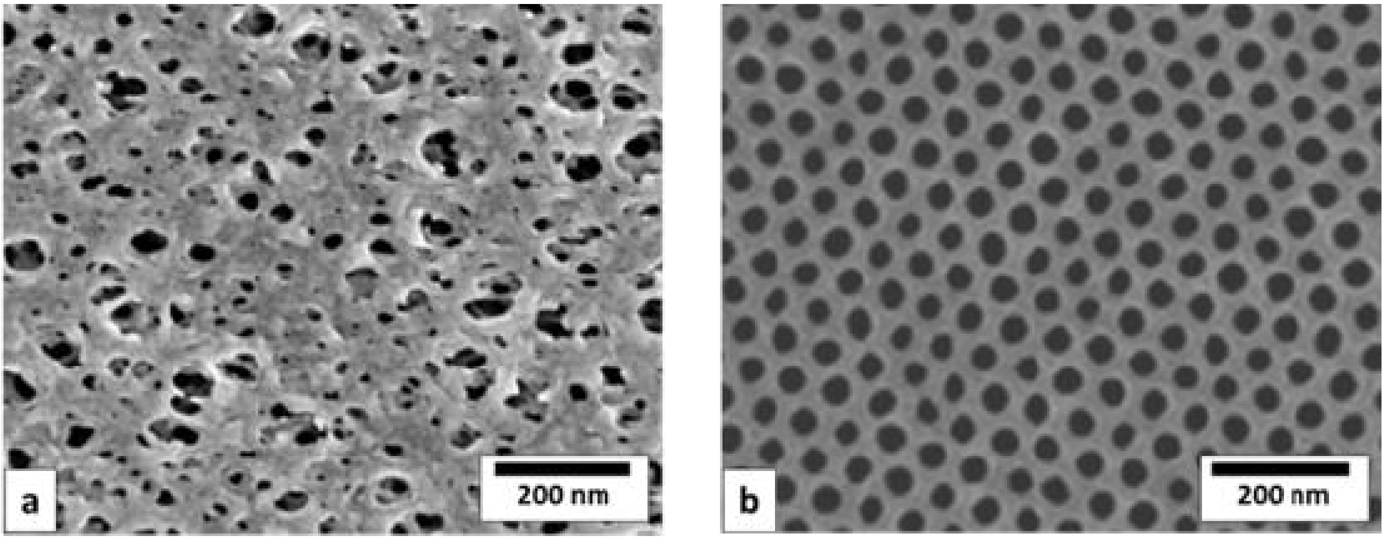

Figure 1: Surface pore structure of (a) a conventional porous support, and (b) an isoporous support.

The probability of successfully producing isoporous supports at commercial scale is high. The method to be used is very similar to existing methods for the manufacture of conventional supports. Moreover, the isoporous support, while of great importance, does not perform the actual separation, which means the occasional pore defects or misalignments are able to be tolerated. This is unlike the ultrafiltration and nanofiltration applications that are the traditional focus of isoporous membrane development.

The project team has prepared many support membranes using the Polystyrene-b-Poly-4-vinylpyridine (BCP1) polymer and has used scanning electron microscopes (SEMs) to evaluate the structures obtained. It is not easy to create the very perfect isoporous surfaces that are reported in the literature for these block copolymers. These surfaces likely represent a few out of many attempts, with the unsuccessful attempts not being reported. However, in the current work, perfect isoporous surfaces are not required; only surfaces that are an improvement over the conventional support membranes are needed. Figure 2 shows the top surface of a BCP1 support that by no means is perfectly isoporous but is expected to be a better support membrane than the conventional support made by MTR, of which a surface SEM is shown in the inset.

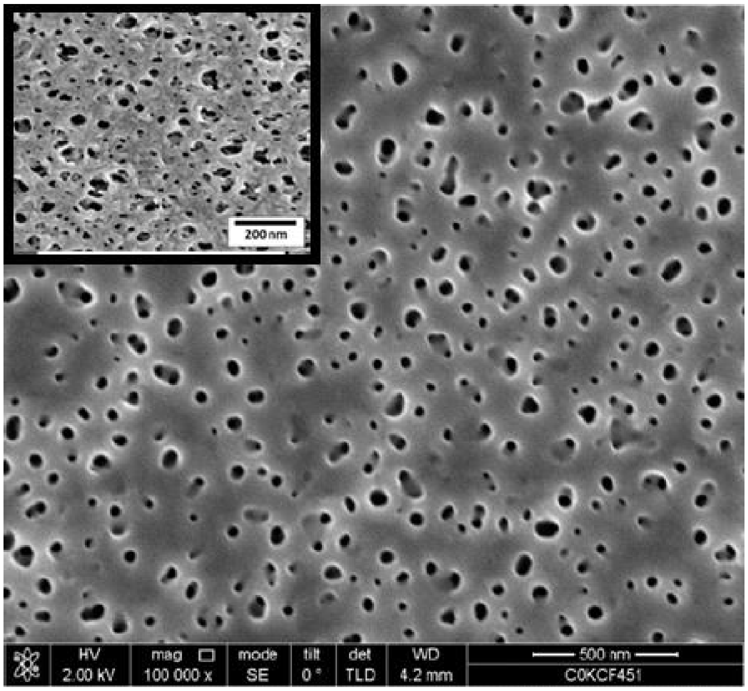

Figure 2: Top surface of a BCP1 support membrane. The inset is a conventional support.

The second development within this project is building on materials research carried out at the University of New York at Buffalo (NYUB), where materials have been identified that, in the form of films, have shown the potential to double the mixed-gas selectivity of the Polaris membrane, albeit at the expense of permeability. Variations of the materials will be synthesized at NYUB, and MTR will produce and test composite membranes using both conventional porous supports and the novel isoporous supports. It is expected that by using the isoporous supports, composite membranes can be produced that are significantly more selective than the current Polaris membrane without increasing the membrane area required.

Recently, the research group at NYUB has developed a new series of copolymers based on poly(1,3 dioxolane), which has the highest ether-oxygen (O)/carbon (C) ratio of any known chemical structure and significantly higher than polyethylene oxide (PEO) (O/C ratio of 0.67 versus 0.5 for PEO). Initial work has confirmed that the higher ether-oxygen content leads to superior CO_2/N_2 separation properties. In the proposed project, a series of PDXLA-co-PDXLEA materials will be thoroughly evaluated with simulated flue gas at various temperatures, pressures, and compositions.

Some of the new materials developed at NYUB are 25 to 50% less permeable than the Polaris polymer but have shown mixed-gas selectivities for CO_2 over N_2 as high as 50 at temperatures between 50 and 60^{o}C. This mixture selectivity is nearly double what Polaris would give at this temperature. Figure 3 compares the predicted performance of these materials coated directly on an isoporous support with Polaris performance. The data point on the PPDXLA curves represents the target performance for the new Polaris high selectivity (HS). This type of performance is well-suited for the sweep step in MTR's patented process design.

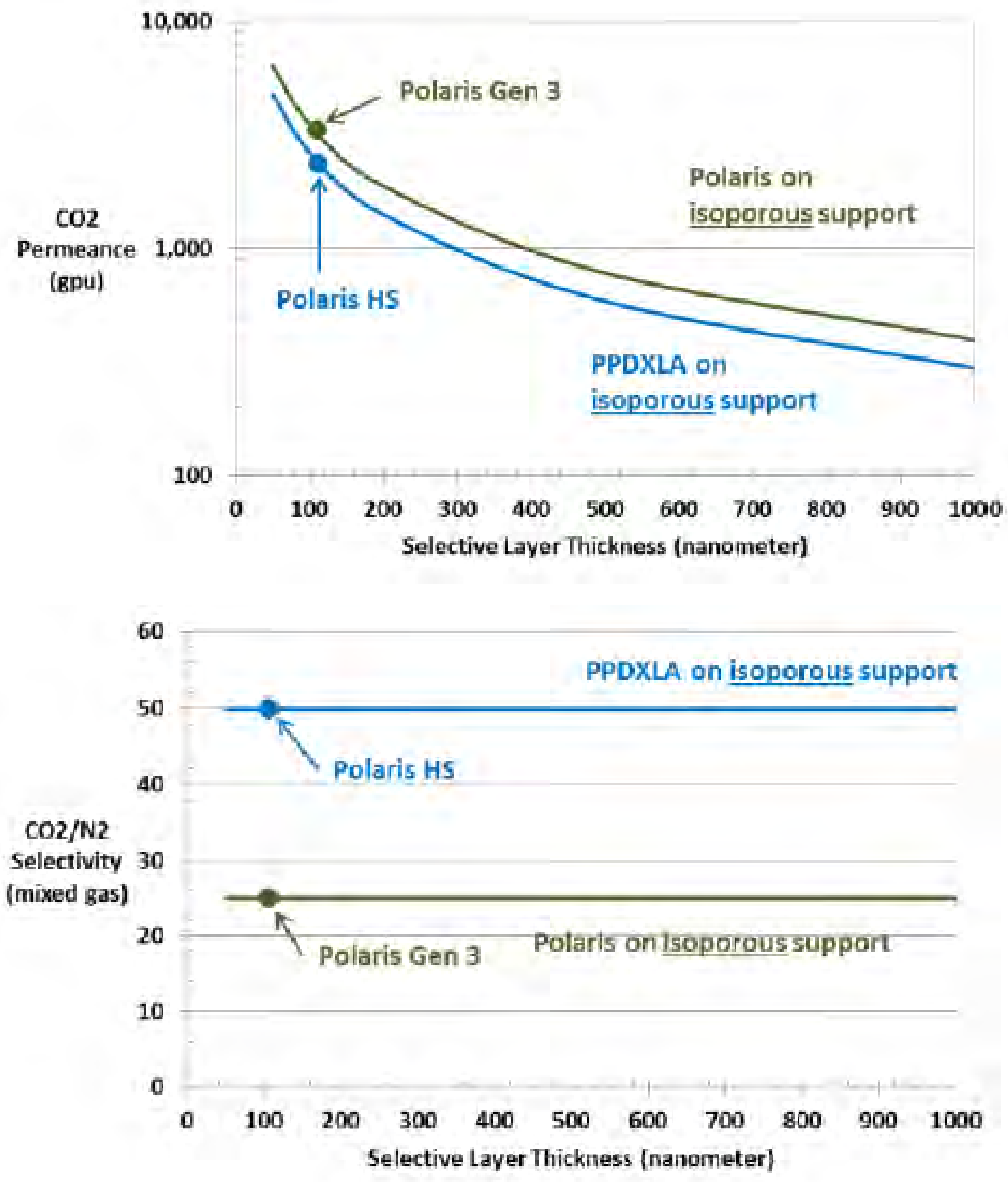

Figure 3: (a) Mixed-gas CO_2 permeance and (b) CO_2/N_2 selectivity as a function of selective layer thickness for Polaris™ and PPDXLA on an isoporous support.

The research group at NYUB is focused on the synthesis of polymers containing high ether-oxygen content for CO_2/N_2 separation. The production of polymers is optimized and scaled-up gradually. The polymers with the most promising properties are delivered to MTR for the production of thin-film composite membranes and then bench-scale membrane modules.

Composite membranes are prepared by coating selective layers onto the isoporous support produced. The selective materials are (1) MTR's Polaris formulation and (2) the selective materials to be developed by NYUB. Composite membranes are characterized first in pure-gas permeation experiments with CO_2 and N_2. Promising membranes are tested more extensively, including pure-gas permeation at different pressures and temperatures, and experiments with $CO_2/N_2/O_2$ mixtures representative of coal-derived flue gas. The coating step with Polaris is straightforward, as MTR has considerable experience with this material. More development and optimization work is required for the newly developed materials.

The very high permeance membranes under development require a redesign of the feed and permeate channels in the MTR planar membrane module. A few options to reduce pressure-drop in those channels are being developed. A summary of the target process parameters is shown in Table 1, while the capture economics data is shown in Table 2.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	planar	planar
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	10,000+ hrs (coal)	10,000+ hrs (coal)
Manufacturing Cost for Membrane Material	\$/m^2	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	Type 1: 4,000 Type 2: 3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	60	Type 1: 25 Type 2: 50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	54	43
Cost of Carbon Avoided	$/tonne CO_2	97	80
Capital Expenditures	$/MWhr	23.9	18.4
Operating Expenditures	$/MWhr	25.9	22.2
Cost of Electricity	$/MWhr	50	50

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation of individual components through the Polaris membrane is driven by partial pressure differences across the membrane generated by a permeate vacuum.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is unknown.

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown.

Membrane Replacement Requirements – Membrane lifetime is estimated at three years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid.

technology advantages

- The novel isoporous supports increases the CO_2 permeance (up to 4,000 GPU).
- The novel membrane selective layer material nearly doubles the CO_2/N_2 selectivity compared to membranes that use Polaris selective material.
- The two-stage capture process allows for high CO_2 capture rates and a high-purity product.
- The selective recycle of CO_2 to the boiler using the air sweep stream increases the CO_2 concentration in flue gas, reducing capital and operating expenditures.

R&D challenges

- Producing dual layer isoporous supports.
- Scale-up of polymer synthesis of improved selective layer materials.
- Tailoring the MTR coating techniques to the new NYUB materials.
- Producing defect-free top layers.

status

MTR continued to vary casting formulations and conditions to identify promising support membrane structures. Membranes prepared from new selective layer materials synthesized by NYUB show pure-gas CO_2/N_2 selectivity up to 89, which is considerably higher than conventional Polaris membranes (CO_2/N_2 selectivity = 50) and demonstrates the potential of this approach. Budget period two (BP2) tasks are nearly complete, and an initial TEA reveals that base CO_2 capture costs can be reduced by 14% with the selected BP2 membranes.

available reports/technical papers/presentations

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," Kickoff meeting presentation, Pittsburgh, PA, September 2018. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," presented at the 2021 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/projects/files/Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture.pdf*.

Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture

primary project goal

Gas Technology Institute (GTI) is developing a transformational graphene oxide (GO)-based membrane process that can be installed in a new or retrofitted into an existing pulverized coal or natural gas power plant for carbon dioxide (CO_2) capture ready for demonstration by 2030. The expected product from this project will be a compact, GO-based membrane prototype system capable of achieving at least 70% CO_2 removal with a single-stage process and 90% CO_2 removal with a two-stage process. The system will be tested over an extended duration on actual flue gas at GTI and the National Carbon Capture Center (NCCC).

technical goals

- Scale-up the GO-based membranes to 50 to 100 cm^2 area and demonstrate that the scaled membranes show CO_2/nitrogen (N_2) selectivity ≥200 and CO_2 permeance ≥1,000 gas permeation units (GPU) for the high-selectivity membranes (designated as GO-1 membranes), and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the high-flux membranes (designated as GO-2 membranes).
- Perform 100 hours of stability testing to demonstrate the CO_2 permeance and CO_2/N_2 selectivity decrease by less than 10% in the presence of flue gas contaminants (oxygen [O_2], sulfur oxide [SO_X], nitrogen oxide [NO_X]).
- Scale-up the GO-based membranes to 500 to 1,000 cm^2 area and demonstrate that the scaled membranes show CO_2/N_2 selectivity ≥200 and CO_2 permeance ≥1,000 GPU for the GO-1, and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the GO-2.
- Achieve 95% CO_2 purity by integrating the GO-1 and GO-2 membranes in a skid (designated as GO^2) for both natural gas and coal-derived flue gases.
- Perform a techno-economic analysis (TEA) to validate that the cost of electricity (COE) is 30% less than the U.S. Department of Energy (DOE) baseline CO_2 capture approach.

technical content

GTI is developing GO-based membranes for CO_2 capture from flue gases. The high-selectivity membranes (GO-1) show CO_2 permeances as high as 1,020 GPU with a CO_2/N_2 selectivity of 680, which is much higher than state-of-the-art membranes. In addition, GTI is also developing high-flux membranes (GO-2) with CO_2 permeance as high as 2,500 GPU using GO quantum dots (GOQD) as a membrane building block. The transformational GO-based membrane process integrates the GO-1 and GO-2 membranes (GO^2), offering a new opportunity to explore further reductions in the cost of CO_2 capture.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membrane

project focus:
Graphene Oxide Membranes for Coal-Derived Flue Gases

participant:
Gas Technology Institute

project number:
FE0031598

predecessor project:
FE0026383

NETL project manager:
Dustin Brown
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principal investigator:
Shiguang Li
Gas Technology Institute
shiguang.li@gastechnology.org

partners:
Rensselaer Polytechnic Institute; The Ohio State University; Trimeric Corporation

start date:
06.01.2018

percent complete:
75%

Graphene-based materials, such as graphene and GO (Figure 1), have been considered as next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux. The feasibility of using a vacuum filtration process to fabricate ultrathin GO membranes (thickness of ~1.8 nm) has been demonstrated. It was observed that the molecular-sized pores of structural defects on GO flakes could serve as a transport pathway for selective gas separations.

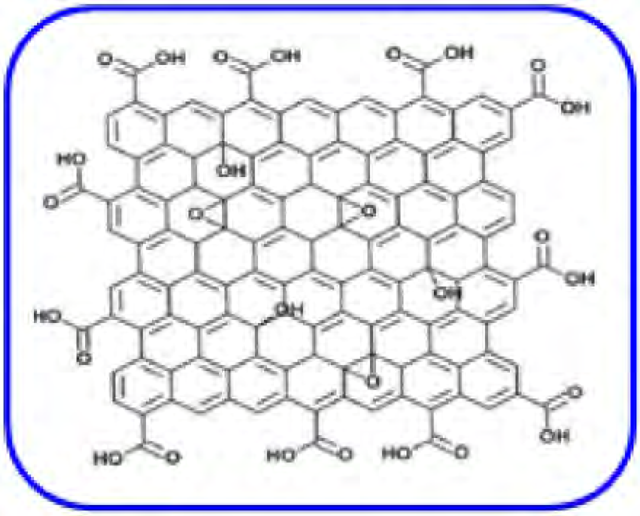

Figure 1: Chemical structural model of GO.

Because of the different morphologies of GO and GOQDs, ultrathin membranes (less than 20 nm) composed of these two different building blocks are expected to have different nanostructures. Figure 2 shows different membrane nanostructures of GO-1 and GO-2 membranes and the proposed transport pathways.

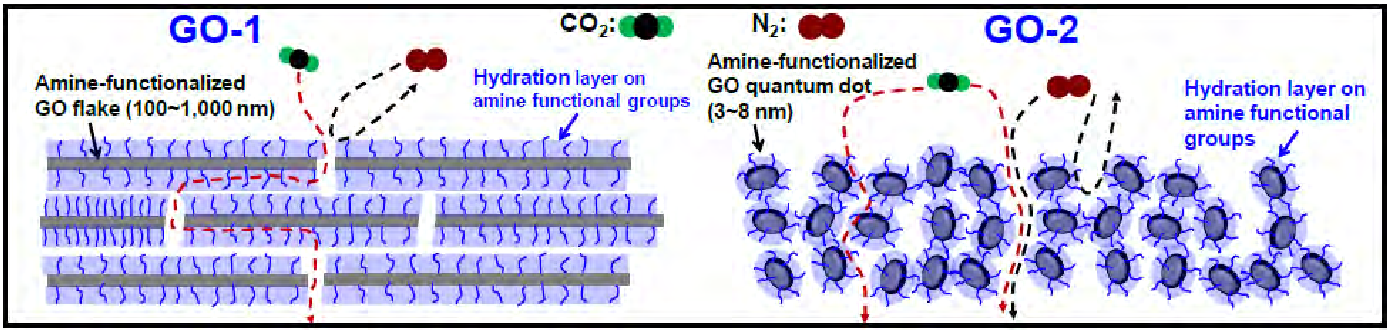

Figure 2: Membrane nanostructures of GO-1 and GO-2 membranes and proposed CO_2 separation mechanisms.

Large GO flakes (greater than 100 nm) with high aspect ratio of lateral size to the flake thickness typically led to regular and uniform lamellar structure (GO-1, left in Figure 2) with a negligible quantity of defects after hydration of surface functional amine groups with water in the flue gas. As a result, CO_2 molecules can quickly transport through the membrane by a facilitated transport mechanism via reaction with amine ($CO_2 + R\text{-}NH_2 \leftrightarrow R\text{-}NH_3^+ + HCO_3^-$) and block the permeation of N_2 molecules. Therefore, GO-1 membranes have moderate CO_2 permeance but high CO_2/N_2 selectivity. In contrast, in GO-2 membranes, the small GOQDs may form a randomly packed nanostructure (right in Figure 2) containing defects that cannot be effectively sealed by the hydration layer. These defects greatly increase the CO_2 permeance, but also decrease the selectivity. Therefore, GO-2 membranes are expected to have high CO_2 permeance but lower CO_2/N_2 selectivity compared to the GO-1 membranes.

In addition to the hollow fiber GO-based membranes, the project team demonstrated for the first time an easy, fast, and scalable printing method with advanced computational controls to deposit ultrathin, high-quality GO-based membranes on a polymeric support for gas separation. A commercial ink cartridge was used to hold an appropriate GO dispersion for printing (Figure 3a). Using only GO "ink," ultrathin GO membranes for highly effective water nanofiltration have been printed. To promote membrane separation performance for a CO_2/N_2 mixture, an extra cartridge was added that holds various amine solutions, such as ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA), to increase both CO_2 permeance and CO_2/N_2 selectivity (Figure 3b). Uniform GO coatings with well-controlled thickness and a membrane area as large as 225 cm^2 have been printed (Figure 3c). Figure 3d shows a typical cross-sectional scanning electron microscopy (SEM) of the printed membrane. Figure 3e indicates the thicknesses of the printed membranes are between 6 and 60 nm and can be well-controlled by the GO concentration.

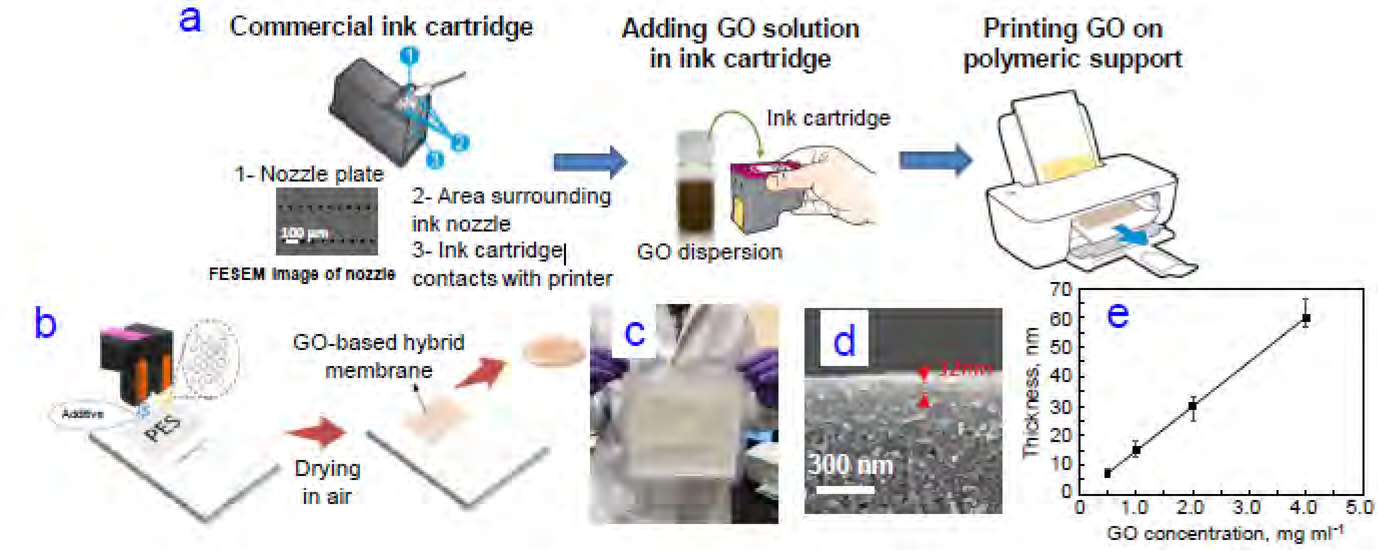

Figure 3: (a) Schematics of GO membrane fabrication by inkjet printing; (b) GO-based membrane preparation by printing from two cartridges containing GO ink and additives; (c) a picture of a printed GO membrane (15 cm × 15 cm); (d) cross-sectional SEM of the membrane; (e) dependence of membrane thickness on GO ink concentration.

The project team prepared GO-based flat-sheet membranes on a polyether sulfone (PES) substrate by printing. The resulting membrane was sealed in a plate-and-frame module for characterization and CO_2/N_2 separation testing. The process parameters for the membranes developed are given in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Graphene Oxide	
Materials of Fabrication for Support Layer	—	Polyether sulfone	
Nominal Thickness of Selective Layer	μm	0.002-0.05 for GO-1 0.005-0.1 for GO-2	0.002-0.02 for GO-1 0.005-0.05 for GO-2
Membrane Geometry	—	Hollow fiber and flat sheet	Hollow fiber and flat sheet
Max Trans-Membrane Pressure	bar	<5	1
Hours Tested without Significant Degradation	—	20	>200 (actual flue gas)
Manufacturing Cost for Membrane Material	$/$m^2$	TBD	TBD
Membrane Performance			
Temperature	°C	80 for GO-1 70 for GO-2	65
CO_2 Pressure Normalized Flux	GPU	1,020 for GO-1 2,500 for GO-2	1,000 for GO-1 2,500 for GO-2
CO_2/H_2O Selectivity	—	1/10 for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
CO_2/N_2 Selectivity	—	680 for GO-1 >30 for GO-2	>200 for GO-1 >20 for GO-2

CO_2/SO_2 Selectivity	—	N/A for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
Type of Measurement	—	mixed gas	mixed gas

Proposed Module Design		(for equipment developers)
Flow Arrangement	—	Crossflow
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	CO_2-rich permeate
Flue Gas Flowrate	kg/hr	TBD
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-90%, >95%, TBD
Pressure Drops Shell/Tube Side	psi/m	Feed and permeate: <1.5

The project team coated GO-based membranes on 50- to 100-cm^2 PES porous hollow-fiber modules by a vacuum filtration process. The sub-recipient systematically synthesized and optimized single-layered GO flakes via different GO synthesis methods. A variety of equipment was used to characterize the membrane morphology, thickness, composition, and structural defects density. The CO_2/N_2 separation properties were measured using an existing laboratory-scale testing system and simulated flue gas.

For coal-fired flue gas, the proposed GO^2 technology is designed to capture 90% CO_2 with greater than 95% CO_2 purity. The system will be installed downstream of flue gas desulfurization (FGD), as shown in Figure 4. It is a compact, stand-alone, membrane-based process, enabling easy integration into the power plant. For the TEA, the data for the current research and development (R&D) values is shown in Table 2.

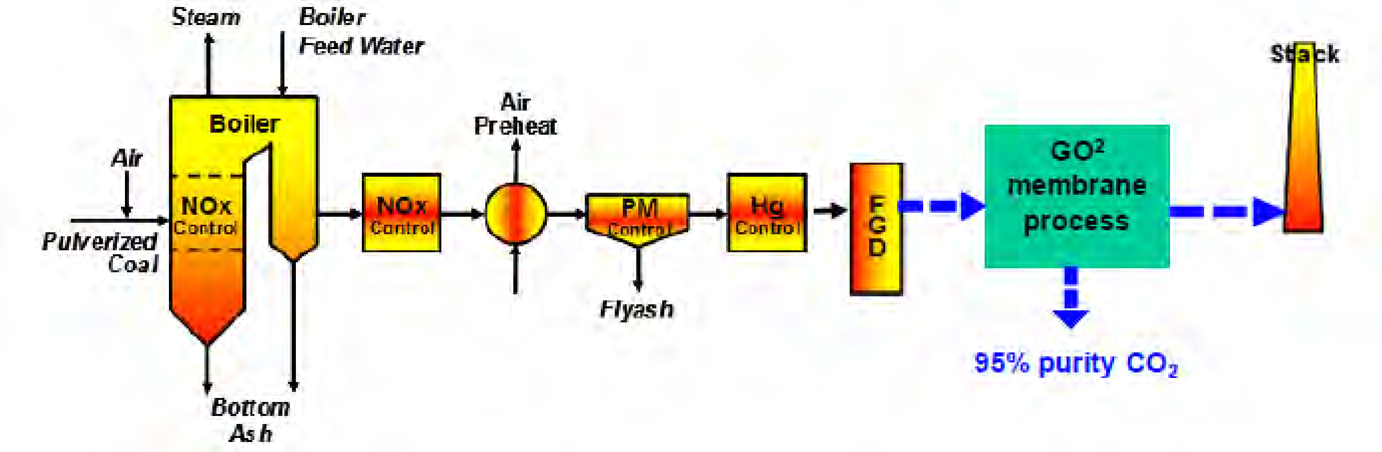

Figure 4: Process flow diagram for the proposed GO^2 process for CO_2 capture.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value*	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	NA	30
Cost of Carbon Avoided	\$/tonne CO_2	NA	NA
Capital Expenditures	\$/MWhr	NA	NA
Operating Expenditures	\$/MWhr	NA	NA
Cost of Electricity	\$/MWhr	NA	93.24

*** Current values are not available (NA). Techno-economic analysis will be performed at the end of the project under Task 10**

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – A vacuum pump is used on the permeate side to provide a vacuum of 2.9 pounds per square inch absolute (psia; 0.2 bar). Because the GO-based membranes are highly water-permeable, the water vapor in the flue gas permeates through the membrane and lowers the partial pressure of CO_2 in the permeate side. Thus, the applied vacuum provides enough driving force for CO_2 permeation. The CO_2-depleted residue leaving the GO-1 unit is sent to a second membrane unit, GO-2, which also uses a vacuum on the permeate side to create the driving force for separation.

Contaminant Resistance – GO is typically prepared under strong acid and oxidation conditions in an aqueous solution, so it is expected to be very stable under these harsh conditions. Additionally, GO is hydrothermally stable at 150°C and has good chemical stability and mechanical strength. Therefore, GO is expected to be stable under flue gas conditions and with flue gas contaminants, such as nitrogen dioxide (NO_2), SO_X, etc.

Flue Gas Pretreatment Requirements – The proposed GO^2 system will be installed downstream of FGD.

Membrane Replacement Requirements – To be determined.

Waste Streams Generated – No waste streams are generated. The GO-based membranes are selective for water (H_2O) over CO_2, and the proposed GO^2 technology can recover the water vapor from the permeate streams. The recovered, mineral-free, high-purity water can be reused by the power plant.

technology advantages

- The technology achieves high CO_2 capture rates (≥70%) with 95% CO_2 purity.
- The water-permeable feature of the GO membrane overcomes the process pressure limitation issue, enhancing mass transfer.
- GO membranes have high thermal/chemical stability and mechanical strength.
- Graphene-based materials such as GO have been considered next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux.
- GTI's printing method for GO membrane formation has several advantages, including:
    - o Low-cost, fast, and scalable deposition of ultrathin GO-based membranes.
    - o Capability of controlling coating properties by controlling printing parameters.
    - o High utilization efficiency of GO material without waste.

o Flexibility of forming GO-hybrid coatings by introducing desired additives.

R&D challenges

- When scaling-up GO-based membranes, the CO_2 permeance and/or CO_2/N_2 selectivity may not scale with size.
- There is risk that membrane sealing issues will be encountered in the development process.
- The commercial PES substrate quality is not currently sufficiently high for scale-up of GO-based membranes.

status

Budget Period 2 tasks are currently underway. GO membranes are being scaled to 1,000 cm^2. After scaling, they will be subjected to stability tests for 100 hours. Concurrently, a GO^2 system will be constructed for the purposes of testing the membranes at bench-scale at NCCC.

available reports/technical papers/presentations

Li, S., 2021, “Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture.” Presented at the 2021 NETL Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Li_1.pdf*.

Li, Shiguang, et al., 2018, “Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture,” presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://netl.doe.gov/sites/default/files/netl-file/S-Li1-GTI-Graphene-Oxide-based-Membrane.pdf*.

Li, S.; Xu, W.; Meyer, H.; Yu, M.; Zhang, S.; Zhou, F.; Ding, Y.; Sexton, A.; Sachde, D.; Biggott, B., 2020, “Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture.” Final Scientific/Technical Report. Report No. GTI 21881. DOE Award No. DE-FE0026383. *https://www.osti.gov/servlets/purl/1750959*.

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Li, Shiguang, et al. “Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture,” presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/S-Li-GTI-Hybrid-Membrane-Process.pdf*.

Li, Shiguang, et al. “Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture,” presented at the BP1 Review Meeting, Pittsburgh, PA, March 2017.

Li, Shiguang, et al. “Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture,” presented at the presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/S-Li-GTI-Go-Peek-Hybrid-Membrane-Process.pdf*.

Li, Shiguang, et al. “Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture,” presented at the project kickoff meeting, Pittsburgh, PA, December 2015.

Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas

primary project goals

The Ohio State University (OSU), along with its partners Gas Technology Institute, the National Carbon Capture Center (NCCC), and American Electric Power, is developing a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture carbon dioxide (CO_2) from flue gas. The project goal is to achieve 60 to 90% capture of CO_2 with greater than 95% CO_2 purity ready for compression to 152 bar (2,200 pounds per square inch [psi]) for storage or enhanced oil recovery and for less than \$30/tonne CO_2 captured.

technical goals

- Optimize and characterize the transformational membrane (including morphology, transport properties, and stability).
- Synthesize an improved polymer support with a CO_2 permeance greater than 23,000 gas permeation units (GPU) for the membrane.
- Develop a polymeric composite membrane with CO_2 permeance greater than 3,300 GPU and CO_2/nitrogen (N_2) selectivity more than 140 at 77°C.
- Design and construct an integrated bench-scale testing system to be tested at OSU and NCCC.
- Complete a techno-economic analysis (TEA) of the project.

technical content

OSU and its partners are developing a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO_2 from flue gas. Based on density functional theory (DFT) calculations indicating a new carrier with high reactivity with CO_2, OSU will synthesize novel transformational polymer membranes with the new carrier, showing a very high CO_2 permeance of about 3,300 GPU (1 GPU = 10^{-6} cm^3(STP [Standard Temperature and Pressure])/(cm^2/s/cm mercury [Hg]) and a very high CO_2/N_2 selectivity of greater than 140. Optimization of the novel transformational membrane, scale-up of the membrane to a prototype size of about 21 inches wide in continuous roll-to-roll fabrication, and construction and testing of a bench skid for the integrated membrane process will be performed.

For the design of this membrane, OSU is using a cost-effective polyethersulfone (PES) support and coating a thin top layer of the membrane (Figure 1). This membrane design offers a low cost for the membrane element in commercial spiral-wound configuration (less than \$2.00/ft^2 or \$21/m^2). Operating parameters and various properties of the membrane are detailed in Table 1. The prototype membrane is used to fabricate at least six pilot-size membrane modules (each about 20-inch length and 35-m^2 membrane area) for testing with simulated flue gas at OSU and subsequently with actual flue gas at NCCC (Wilsonville, Alabama), using the skid to capture the CO_2 (at 60 to 90%) with at least 95% CO_2 purity (Figure 2). The prototype membrane modules will be in commercial spiral-wound configuration with a minimal pressure drop (less than 0.103 bar/meter or 1.5 psi/meter).

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Polymeric Composite Membranes

participant:
The Ohio State University

project number:
FE00031731

predecessor project:
FE0026919

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partners:
Gas Technology Institute; National Carbon Capture Center; American Electric Power

start date:
07.01.2019

percent complete:
70%

After the skid testing, OSU will determine the identity and concentration of any possible contaminates on the membrane via laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), Fourier transform infrared spectroscopy (FTIR), X-ray photoemission spectrometry (XPS), and nuclear magnetic resonance spectroscopy (NMR). Economic data is shown in Table 2.

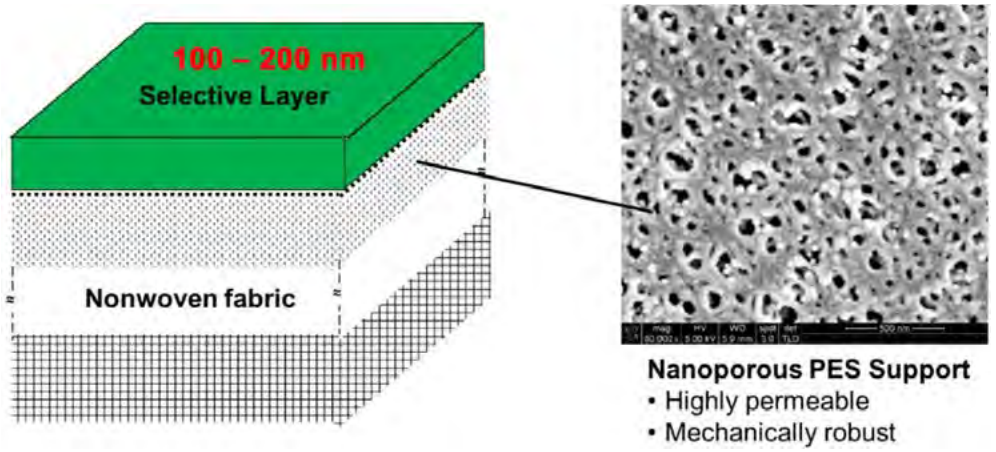

Figure 1: Schematic of thin-film composite membrane consisting of an amine-containing cover layer on a nanoporous PES support.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	170	150–250
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	2,500 hours	500 hours
Manufacturing Cost for Membrane Material	$\$/m^2$	20	20
Membrane Performance			
Temperature	°C	57–77°C	57–77°C
CO_2 Pressure Normalized Flux	GPU	3,670 GPU	>3,300 GPU
CO_2/H_2O Selectivity	—	1	1
CO_2/N_2 Selectivity	—	155	>140
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	spiral-wound	
Packing Density	m^2/m^3	about 2,000	
Permeate-Side Fluid	—	vacuum or retentate recycle	
Flue Gas Flowrate	ft^3/min	10.3	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>60%–90%, >95%, 1 bar	
Pressure Drops Feed/Permeate Side	psi/m	1.5/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	32.3	

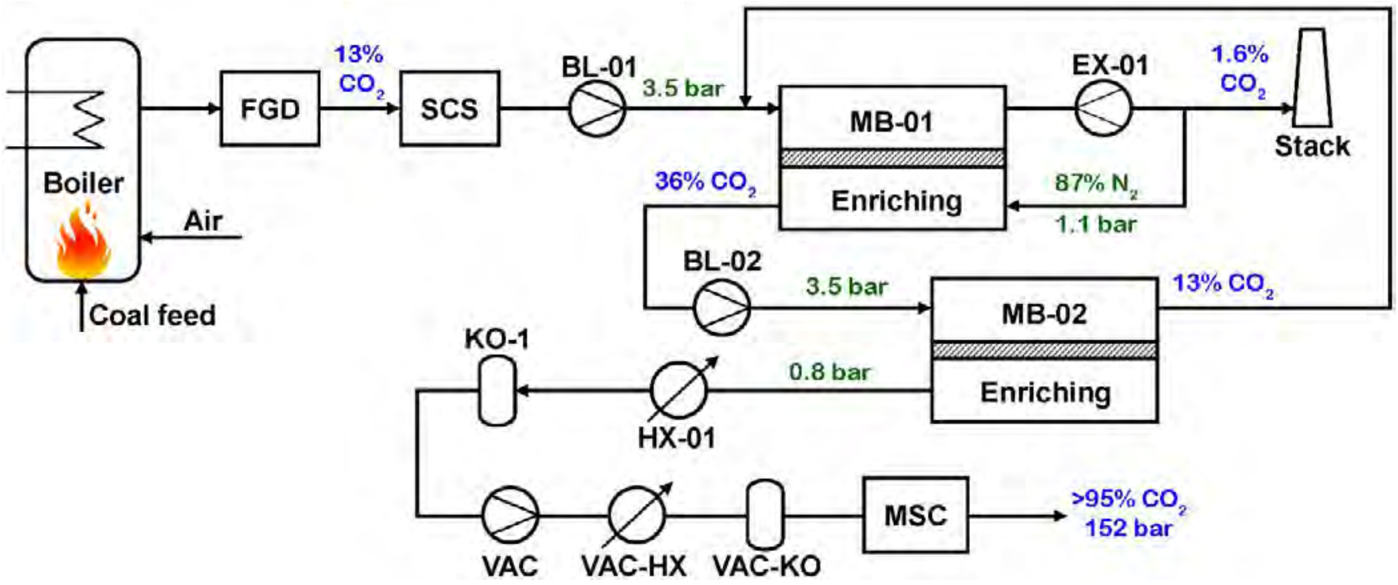

Figure 2: Process concept for two-stage membrane system. Initialisms: FGD = flue gas desulfurization; SCS = SO_2 caustic scrubber; BL = blower; MB = membrane; EX = turbo expander; HX = heat exchanger; KO = knockout; VAC = vacuum pump; MSC = multi-stage compressor.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.3	40.0
Cost of Carbon Avoided	$/tonne CO_2	53.9	55.2
Capital Expenditures	$/MWhr	21.4	22.0
Operating Expenditures	$/MWhr	11.4	12.0
Levelized Cost of Electricity	$/MWhr	100.5	101.0

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Permeate-Side Fluid – Either vacuum or a sweep gas.

Estimated Cost – Basis is m^2 membrane area.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance – Resist up to 3 parts per million volume (ppmv) sulfur dioxide (SO_2).

Flue Gas Pretreatment Requirements – Removal of particulates and SO_2 polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – Nitrogen with water (H_2O), about 1% CO_2, and minor impurities.

Process Design Concept – See Figure 2.

technology advantages

This membrane consists of a thin selective polymer layer on a polymer support so that it can be made efficiently in continuous roll-to-roll manufacturing. The membrane offers high CO_2/N_2 selectivity at greater than 57°C, which does not require flue gas cooling or cryogenic distillation. The simplicity of this membrane design offers a low cost for the membrane element in commercial spiral-wound configurations. If successful, the process can achieve less than \$30/tonne CO_2 for 70% recovery.

R&D challenges

- Membrane stability in the presence of high-level contaminants, such as SO_2 and nitrogen oxide (NO_X).
- Design and fabrication of prototype spiral-wound membrane module with 8-inch diameter.
- Requires two membrane stages.

status

A highly permeable PES support with bicontinuous morphology was developed. The polymer support exhibited a CO_2 permeance of 310,000 GPU, 13 times more permeable than the project target. A thin-film composite membrane containing a novel CO_2 carrier was synthesized and scaled up to 21-inch width. The prototype membrane demonstrated a CO_2 permeance of 3,670 GPU and a CO_2/N_2 selectivity of 155 with simulated flue gas. The scaled-up membrane was successfully rolled into a prototype spiral-wound (SW) membrane module with 8-inch diameter and 35-m^2 membrane area. The SW module demonstrated a CO_2/N_2 separation performance on par with the flat-sheet membrane.

available reports/technical papers/presentations

Ho, W.; Han, Y.; Lin, L-C., "Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas." National Energy Technology Laboratory. Carbon Management and Natural Gas & Oil Research Project Review Meeting. Pittsburgh, PA. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ho_0.pdf*.

R. Pang, K. K. Chen, Y. Han, and W. S. W. Ho, "Highly Permeable Polyethersulfone Substrates with Bicontinuous Structure for Composite Membranes in CO_2/N_2 Separation", Journal of Membrane Science, 612, 118443 (2020).

Ho, W., Han, Y., "Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas," poster presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019.

Ho, W., Han, Y., "Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas," presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Membrane.pdf*.

Rational Development of Novel Metal-Organic Polyhedra-Based Membranes for CO_2 Capture

primary project goal

The State University of New York (SUNY) at Buffalo, along with its partners, is developing solubility-selective mixed matrix membranes (MMMs) comprising highly polar rubbery polymers and soluble metal-organic polyhedra (MOPs) to achieve high carbon dioxide (CO_2) permeance (3,000 gas permeation units [GPU]), high CO_2/nitrogen (N_2) selectivity (75), and CO_2/oxygen (O_2) selectivity (30) at 60°C. Such membranes would outperform currently leading membranes by 50–100%, which can be implemented into Membrane Technology and Research Inc.'s (MTR's) membrane processes and may enable CO_2 capture at less than $30/ton CO_2 from coal power plants.

technical goals

- Develop solubility-selective MMMs comprising polar rubbery polymers and MOPs.
- Develop thin-film composite (TFC) membranes achieving high CO_2 permeance (3,000 GPU) and high CO_2/N_2 selectivity (75) at 60°C.
- Demonstrate separation performance and stability with raw flue gas at the National Carbon Capture Center (NCCC).
- Perform techno-economic analysis (TEA) on the membrane processes.

technical content

The project team is developing transformative solubility-selective MMMs containing MOPs and rubbery polar polymers. These transformative MMMs are built upon three key unique approaches. First, rubbery polymers with CO_2-philicity (and N_2-phobicity) will be designed, in contrast with most of the literature approach in pursuing glassy polymers with strong size-sieving ability. Second, MOPs with strong CO_2 affinity will be designed and added to increase the CO_2/gas solubility selectivity. In contrast to the commonly pursued insoluble metal-organic frameworks (MOFs), these MOPs are discrete nano-cages and soluble in organic solutions, making it easier to prepare TFC membranes with selective layers as thin as 100 nm. Third, the structure of polymers and MOPs can be independently designed with enormous possibilities, which can be accelerated using computational simulation.

A consortium of six organizations with complementary capabilities was assembled to achieve these goals, including University at Buffalo (UB; SUNY–Buffalo), Rensselaer Polytechnic Institute (RPI), California Institute of Technology (Caltech), MTR, NCCC, and Trimeric Corporation (Trimeric). The UB team is conducting fundamental and industrial membrane development and MOP synthesis and application to develop the novel materials, performing laboratory parametric tests, and scaling-up the production. RPI is preparing functionalized polymers and scaling-up the production. Caltech is simulating gas permeation to guide the design of the MMMs. MTR is preparing TFC membranes and bench-

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Mixed Matrix Membranes for Coal-Derived Flue Gas

participant:
State University of New York–Buffalo

project number:
FE0031736

predecessor projects:
N/A

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partners:
Rensselaer Polytechnic Institute; California Institute of Technology; Membrane Technology and Research Inc.; National Carbon Capture Center; Trimeric Corporation

start date:
07.01.2019

percent complete:
55%

scale modules and performing field tests at NCCC. Trimeric is updating the membrane process design and economic analysis based on MTR's patented processes. The endpoint of this project is a field test of bench-scale membrane modules, and a TEA of the newly developed membranes elucidating their potential to meet U.S. Department of Energy's (DOE) goals for CO_2 capture. A graph of the selectivities of the two chosen macromonomers is shown in Figure 1, while a simplified visual perspective of the membrane process is shown in Figure 2. The parameters governing membrane operation are shown in Table 1.

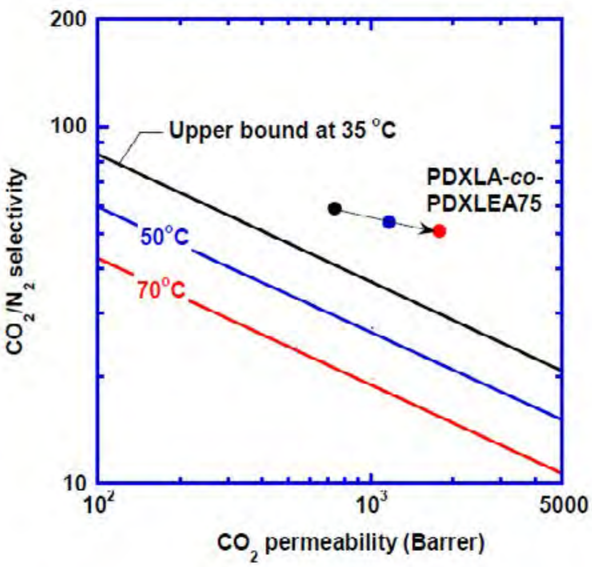

Figure 1: The "rubbery polymers": two macromonomers, poly(1,3-dioxolane) acrylate (PDXLA) and poly(1,3-dioxolane) ethyl ether acrylate (PDXLEA) are highly polar polymers that exhibit CO_2/N_2 separation properties above the upper bound in the Robeson's plot.

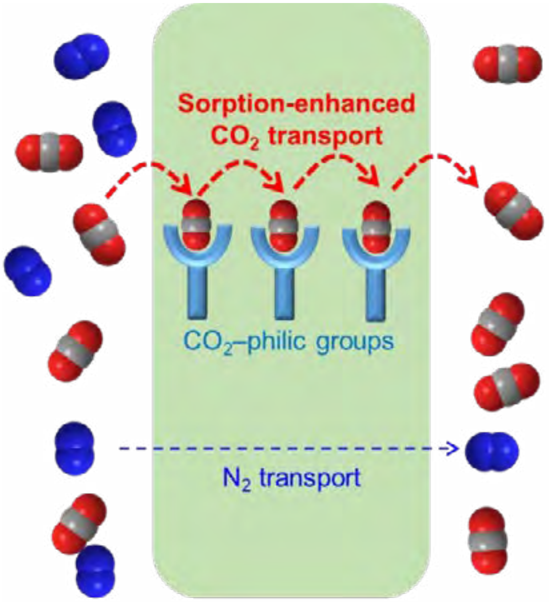

Figure 2: The highly branched amorphous polymers containing poly(1,3-dioxolane) (PDXL) in the branches interact favorably with CO_2, but not N_2, allowing for the design of solubility-selective membrane materials with superior performance for gas separations.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Mixed matrix materials of rubbery polymers and MOP	
Materials of Fabrication for Support Layer	—	Glassy polymers such as PAN, PSf	
Nominal Thickness of Selective Layer	nm	200–1,000	100–300
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	120	500
Membrane Performance			
Temperature	°C	60°C	60°C
CO_2 Pressure Normalized Flux	GPU	1,500–2,000	3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	75
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Mixed gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	300–600	
Shell-Side Fluid	—	feed	
Flue Gas Flowrate	ft^3/min	–	
CO_2 Recovery, Purity, and Pressure	%/%/bar	–	
Pressure Drops Feed/Permeate Side	psi/m	–	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	–	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

MOP – Metal-Organic Polyhedron (singular)/Polyhedra (plural); 2–5-nm-sized molecule with metal bonding sites for CO_2.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} $cm^3/(cm^2 \cdot s \cdot cm$ mercury [Hg]) at 1 atmosphere (atm) and 0°C. For non-linear materials, the dimensional units reported shall be based on flux measured in $cm^3/(cm^2 \cdot s)$ (at 1 atm and 0°C) with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} $kgmol/(m^2 \cdot s \cdot kPa)$ (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities shall be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate stream.

technology advantages

This membrane process builds upon innovative membrane process design using CO_2-selective membranes developed by MTR. If successfully developed, such membranes would outperform current leading membranes by at least 50%.

R&D challenges

This approach of solubility-selective MMMs based on soluble MOPs directly addresses the two key challenges for membranes for CO_2 capture: (a) transport phenomena in new membrane materials, and (b) fabrication and use of the novel membrane systems in effective process designs.

status

The DXL ring opening reactions have been optimized using methanol and ethanol as initiators. New ligands were synthesized to help improve self-assemblies at coordination sites. The synthesis of the PDXLA macromonomer was successfully scaled up to 90g/batch. Further optimization of the monomers continues with the development of new chain-end groups and new compatible MOPs. The PDXLA macromonomer was also successfully polymerized and fabricated into TFC membranes.

available reports/technical papers/presentations

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Metalorganic-Membrane.pdf*.

Lin, H.; Cook, T.; Bae, C.; Wang, Z.; Merkel, T.; Morton, F.; Sexton, A., "Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture (FE0031736)," presented by Haiqing Lin, University of Buffalo, The State University of New York, NETL Project Kickoff Meeting, Morgantown, WV, January 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10761&filename=Aoi+%5b1c%5d+Rational+Development+of+Novel+Metal-Organic+Polyhedra-Based+Membranes+for+CO2+Capture.pdf*

CO_2-Philic Block Copolymers with Intrinsic Microporosity for Post-Combustion CO_2 Capture

primary project goal

In this Phase II Small Business Technology Transfer (STTR) program, Helios-NRG and its partners, the University of Buffalo and TechOpp Consulting, are developing carbon dioxide (CO_2)-philic block copolymers with intrinsic microporosity (BCPIMs) for post-combustion CO_2 capture. The BCPIMs consist of rubbery polyethylene oxide (PEO) and polymerizable metal-organic frameworks (polyMOFs) and have superior CO_2/nitrogen (N_2) separation properties. The materials are being designed, synthesized, and characterized for carbon capture. In Phase I, the team's preliminary results found that the optimized materials achieved CO_2 permeability of at least 2,000 Barrer and CO_2/N_2 selectivity of at least 40; the materials also showed good stability in the presence of water vapor, sulfur oxide (SO_X), and nitrogen oxide (NO_X). Initial techno-economic analysis (TEA) work confirmed the potential of the advanced membranes to achieve the project objective of $30/tonne CO_2 or lower. Phase II efforts are focused on optimizing and scaling-up of the fabrication of thin-film composite (TFC) membranes for CO_2/N_2 separation. These membranes are being tested for long-term membrane resistance to contaminants while using real flue gas, followed by bench-scale module fabrication and performance measurements over a range of operating conditions.

technical goals

- Develop BCPIMs exhibiting CO_2 permeability of 2,000 Barrer or above and CO_2/N_2 selectivity of 40 or greater.
- Demonstrate stability of the BCPIMs in the presence of water vapor, SO_X, and NO_X.
- Develop TFC membranes based on BCPIMs; achieve CO_2 permeance greater than 4,500 gas permeation units (GPU) and CO_2/N_2 selectivity greater than 40.
- Develop process cycles incorporating BCPIM membranes with potential to achieve less than $30/ton CO_2.

technical content

In striking contrast to the conventional mixed matrix membranes (MMMs) comprising size-sieving MOFs in glassy polymers, this project is developing scalable membranes based on BCPIMs to achieve superior CO_2/N_2 separation properties. The BCPIMs are micro-phase separated. The continuous phase is based on state-of-the-art amorphous PEO with superior CO_2/N_2 separation property. The discontinuous phase of polymer intrinsic microporosity (PolyIMs) has extremely high gas permeability, dramatically increasing gas permeability without reducing CO_2/N_2 selectivity. More importantly, the configuration of polymers only minimizes the formation of voids between polymers and MOFs in traditional MMMs and allows facile integration into the current membrane manufacturing trains.

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Membranes

project focus:
Composite Membranes Comprised of Block Copolymers for CO_2 Capture

participant:
Helios-NRG LLC

project number:
SC0020730

predecessor projects:
N/A

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partners:
N/A

start date:
06.29.2020

percent complete:
47%

To demonstrate the feasibility, to the project team is preparing two series of copolymers — block copolymers (BCPolyMOFs) derived from polyMOFs and interpenetrating networks (IPNs) containing polymers of intrinsic microporosity (PIMs).

Approach I: Design of PolyMOFs and BCPolyMOFs. First, the MOFs with amine groups on the organic ligand react with methacrylamide groups to graft methacrylate groups. Second, the polyMOFs with methacrylate groups can be copolymerized with propylene glycol methyl ether acetate (PEGMEA) and/or polyethylene glycol diacrylate (PEGDA) via photo- and thermal-polymerization or atom transfer radical polymerization (ATRP). PEGDA also serves as a cross-linker for the curing process. The resulting copolymers have a general chemical structure shown in Figure 1a. The cross-linking scheme is under mild conditions (e.g., room temperature); thus, the MOFs structure is not damaged during synthesis. The MOFs with large pore sizes and high porosity are preferred to provide high gas permeability, and yet they have amine groups to functionalize with the acrylate groups for polymerization.

Approach II: IPNs Containing PIMs. IPNs can be easily prepared by dissolving the PIMs (such as PIM-1 with chemical structure shown in Figure 1b) and the macromonomers of PEGMEA before the polymerization. PIMs can be prepared using widely reported methods in the literature. These polymers can provide a quick indication of the effect of the PIM phase on the CO_2/N_2 separation properties.

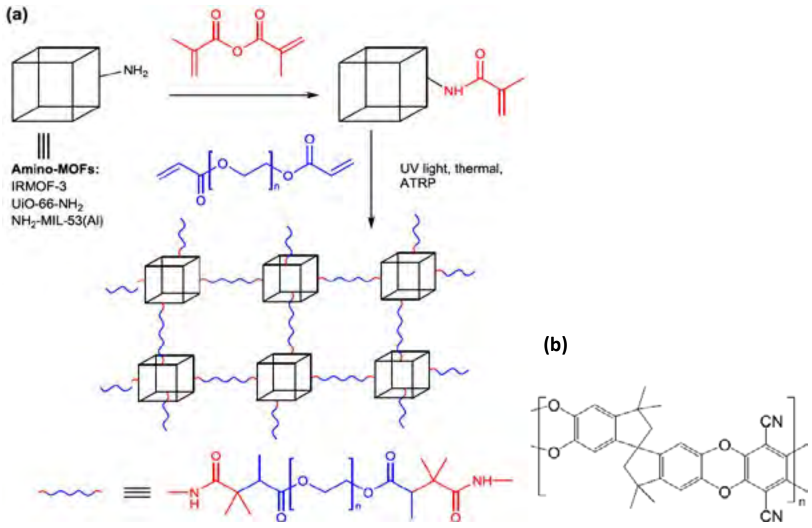

Figure 1: (a) Representative scheme to prepare polyMOFs and BCPolyMOFs, adapted from a reference. (b) PIM-1 chemical structure to be prepared into IPNs.

The project team identified UiO-66-NH_2 as a good candidate for polyMOFs because of its large pore size and high porosity to provide high gas permeability and excellent stability in the humid and acidic environment. It also has amine groups to functionalize with the acrylate groups for polymerization. The project team successfully prepared UiO-66-NH_2 nanoparticles as small as 50 nm (Figure 2a). Figure 2b shows that the reacted UiO-66-NH_2 exhibits the X-ray diffraction (XRD) patterns similar to the pristine ones, indicating that the crystal structure (including pore size and porosity) is not changed by the functionalization.

To prepare BCPolyMOFs, the project team first optimized the polymer matrix to improve the CO_2 permeability. Eighteen-Crown-six with the same ether oxygen content as PEO was added into prepolymer solutions of the PEGDA and PEGMEA (20/80) before the photopolymerization. Increasing the crown ether content significantly increased the CO_2 permeability without a significant effect on the CO_2/N_2 selectivity. For example, adding 50 wt% of crown ether in Cross-linked poly(ethylene oxide) (XLPEO) increases CO_2 permeability from 580 to 1,100 Barrer while retaining CO_2/N_2 selectivity of 43. Such an increase can be ascribed to the decrease in the glass transition temperature (Tg), indicating the increased flexibility of polymer chains and thus gas diffusivity.

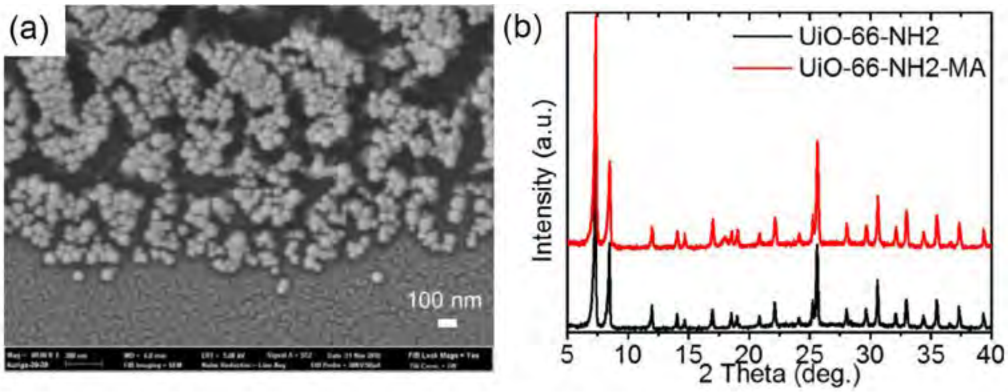

Figure 2: (a) SEM image of UiO-66-NH_2 nanoparticles; (b) XRD patterns of nanoparticles before and after the functionalization.

Second, the prepared UiO-66-NH_2 nanoparticles were also incorporated into the prepolymer solutions containing PEGDA, PEGMEA, and crown ether before the photopolymerization. Adding 1.0 wt% of MOF dramatically increased CO_2 permeability from 580 Barrer in XLPEO to 770 Barrer and from 1,100 Barrer in the blend containing 50% XLPEO and 50% crown ether (XLPEO-CE50) to 2,200 Barrer, as shown in Figure 3a. The increase in CO_2 permeability by adding the MOFs does not decrease CO_2/N_2 selectivity (Figure 3b). The BCPolyMOFs containing 1% MOFs in the XLPEO-CE50 (XLPEO-CE50-MOF1) showed the best CO_2/N_2 separation performance and were further evaluated with a gas mixture (20% CO_2/80% N_2) at different temperatures. Mixed-gas separation properties are more or less consistent with the pure-gas properties. Increasing the temperature increases CO_2 permeability and decreases CO_2/N_2 selectivity. Although there is a tradeoff between permeability and selectivity in operating these membranes, the BCPolyMOFs show CO_2 permeability of 2,200 Barrer and CO_2/N_2 selectivity of 50 at 35°C, which meets the targets for the project.

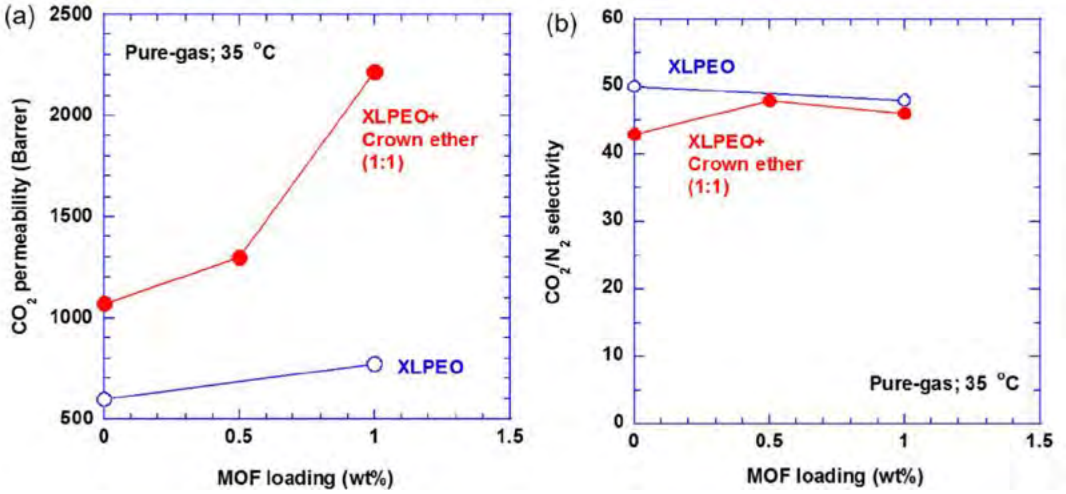

Figure 3: Effect of the MOF loading on (a) CO_2 permeability; (b) CO_2/N_2 selectivity at 35°C and 30 psig.

To demonstrate the promise of these new materials for practical applications, the project team prepared TFC membranes, as shown in Figure 4. The selective layer based on the BCPIMs provides the CO_2/N_2 separation properties. The gutter layer provides a smooth surface for the selective layer to deposit and provides extremely high gas permeance to channel the permeating gas to the open pores of the substrate. The porous support also provides mechanical properties needed for handling.

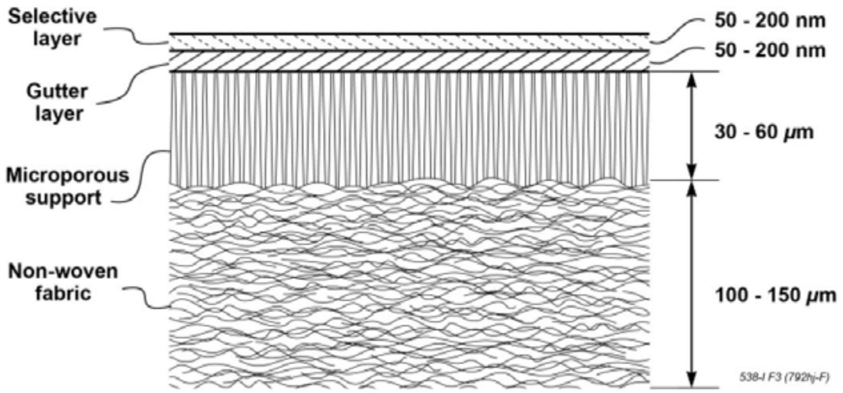

Figure 4: Schematic of TFC membranes comprising a selective layer, gutter layer, and porous support.

The project team identified polysulfone (PSF) ultrafiltration (UF) membranes as the porous support and polydimethylsiloxane (PDMS) with a CO_2 permeability of 3,000 Barrer and N_2 permeability of 300 Barrer as the gutter layer. PEGMEA was polymerized using ATRP, which was then coated onto the gutter layer using a dip-coater. The PEO layer increases the CO_2/N_2 selectivity compared with the PDMS layer. The performance of CO_2 permeance ranging from 630–2,500 GPU and CO_2/N_2 selectivity ranging from 43–30 is comparable with the leading membranes, demonstrating their potential. To improve the hydrophilicity of the gutter layer, the project team used polydopamine (PDA) to modify the PDMS gutter layer surface. After the PDA modification, the PDA/PDMS gutter layer shows water contact angle 60° and CO_2 permeance of 6,500 GPU. With the same coating solution, the membrane based on PDA/PDMS shows higher CO_2 permeance and higher CO_2/N_2 selectivity than that based on PDMS.

technology advantages

- Advanced materials with CO_2 permeability of 2,000 Barrer and CO_2/N_2 selectivity of 40.
- Material stability in the presence of acid gases.

R&D challenges

- Scale-up of TFC membrane fabrication.

status

Helios-NRG has developed a TFC membrane with CO_2 permeance = 4,500 GPU and CO_2/N_2 selectivity = 40 at 35–60°C. Current efforts include scaling-up TFC membrane fabrication, validating resistance to flue gas contaminates in long-term testing, and fabricating small modules and validating performance in process tests in preparation for testing at the National Carbon Capture Center (NCCC).

available reports/technical papers/presentations

Ravi Prasad, Haiqing Lin, "CO_2-Philic Block Copolymers with Intrinsic Microporosity (BCPIMs) for Post Combustion CO_2 Capture," Phase II Project kickoff meeting presentation, Pittsburgh, PA, November 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12345&filename=CO2-Philic+Block+Copolymers+with+Intrinsic+Microporosity+(BCPIMs)+for+Post+Combustion+CO2+Capture.pdf*.

High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing

primary project goal

Lawrence Livermore National Laboratory (LLNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, has designed and fabricated high-efficiency reactors supporting advanced sorbents, solvents, or membranes for transformational carbon capture. An integrated design process coupling computational design optimization with additive manufacturing (AM) was used to create novel reactor geometries customized for new carbon dioxide (CO_2) capture materials.

technical goals

- Assess new reactor geometries and identify design principles.
- Assess AM for each reactor type.
- Identify the most promising reactor class (sorbent, solvent, or membrane) for the next phase of development.
- Design and test the first-generation bench-scale reactor.
- Evaluate a small-scale integrated prototype of the first-generation reactor design with simulated flue gas.
- Design and test a second-generation bench-scale reactor.
- Design an integrated prototype of the second-generation reactor concept.

technical content

LLNL designed high-efficiency reactors to support advanced sorbents, solvents, or membranes for CO_2 capture. An integrated design process utilizing computational design optimization combined with AM was utilized to create new reactor geometries designed for advanced carbon capture materials resulting in efficient, low-cost carbon capture. The reactors can offer a range of improvements for CO_2 capture, including absorbers and fixed beds with integrated heat exchange, enabled by the unique structure of the triply periodic minimal surfaces (TPMS). They can also enable membrane-based separators with minimal pressure drop and strippers capable of extreme high pressure. The conceptual basis of these novel reactors are hierarchical networks and TPMS, shown in Figure 1. These new geometries were fabricated using AM techniques at LLNL. An example of a TPMS structure fabricated using metal AM at LLNL is shown in Figure 2. The TPMS geometries can be made into structured packings for columns. These TPMS-printed packings provide surface area for solvent and flue gas to interact, and can allow for integrated heat exchange. LLNL has demonstrated printed packings in multiple different plastics, including acrylonitrile butadiene styrene (ABS), high-density polyethylene, polycarbonate, nylon, and acrylic-based photopolymers. An ABS-based packing showing the same geometry as a conventional stainless steel packing is shown in Figure 3.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post Combustion Power Generation PSC

key technology:

Novel Concepts

project focus:

Additively Manufactured High-Efficiency Reactors for Sorbents, Solvents, and Membranes

participant:

Lawrence Livermore National Laboratory

project number:

FWP-FEW0225

predecessor projects:

N/A

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partners:

N/A

start date:

08.01.2017

percent complete:

100%

LLNL evaluated novel geometries and identified the design concepts and principles for these new reactor types. The AM techniques were assessed. The most promising reactor class, either sorbent, solvent, or membrane, was identified to move forward with in the development process. A first-generation reactor was designed, fabricated with the AM techniques, and tested on simulated flue gas at bench scale. Based on the test results, the team designed a more advanced second-generation reactor.

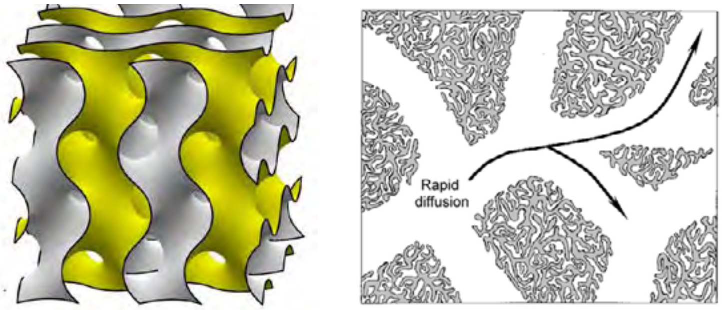


Figure 1: Design features focused on at LLNL: triply periodic minimal surface (left), hierarchical flow channels (right).

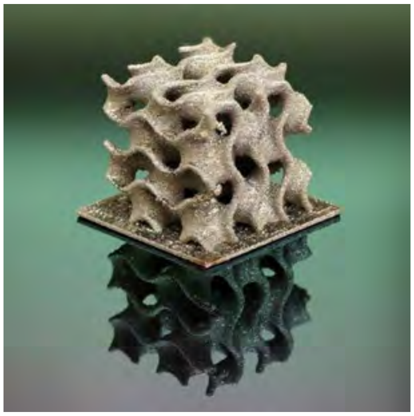


Figure 2: TPMS structure printed using metal AM at LLNL.

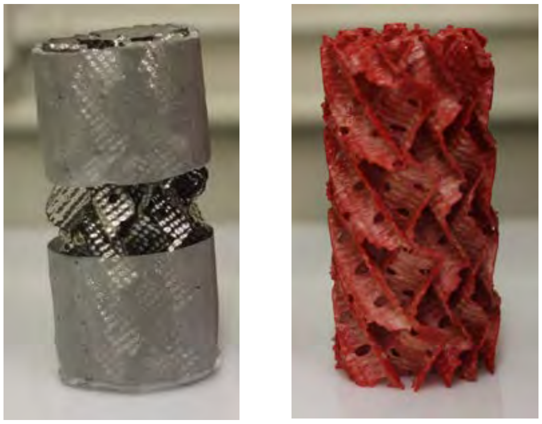


Figure 3: Conventional stainless steel packing (left) and ABS-printed packing (right).

The first-generation reactors were based on a membrane system where flue gas flowed through one side of a TPMS geometry and a solvent flowed through the other, separated by a gas-permeable membrane. Since TPMS reactors were known to have high heat transfer performance, similar advantages were expected in mass transfer reactors. This method of reactor required the development of a CO_2 permeable membrane that could be printed into the TPMS geometry, which was successful and is shown in Figure 4. In this manner, a TPMS mass transport reactor would behave similarly to a heat transfer reactor.

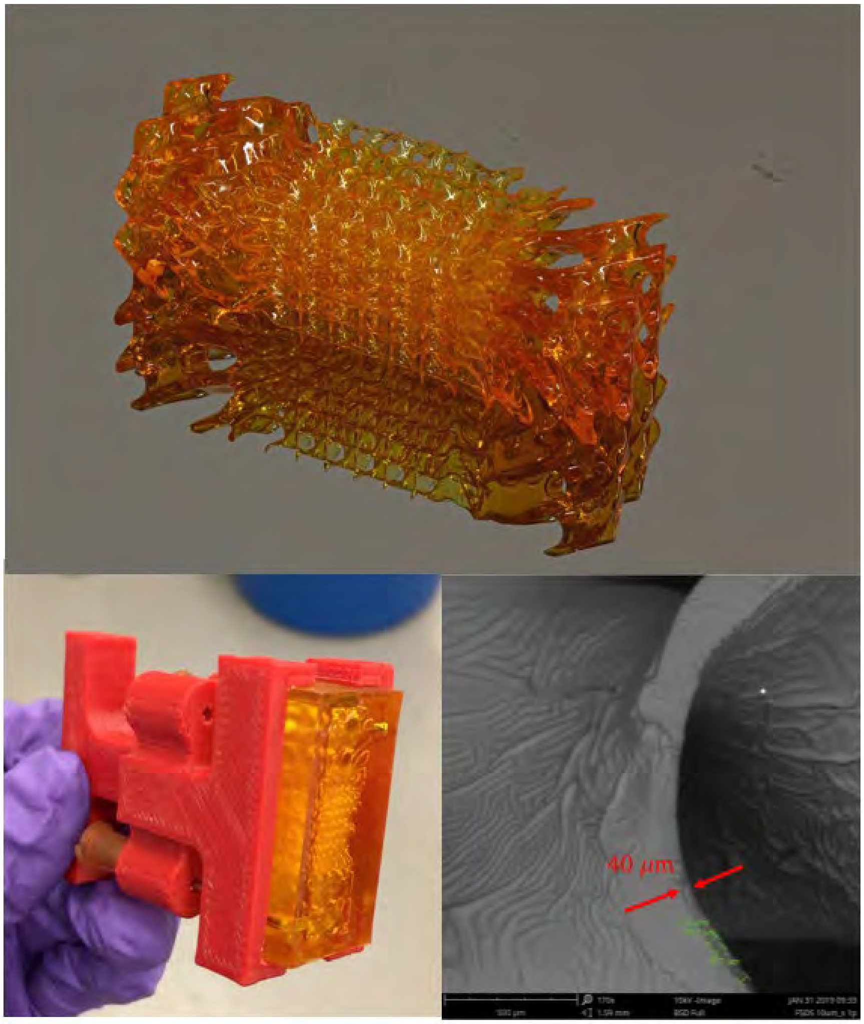


Figure 4: Hierarchically structured TPMS membrane reactor (top). TPMS membrane reactor in holder with fluidic connections (left). Scanning electron microscopy (SEM) image of TPMS membrane reactor (right).

Significant development was necessary to enable the AM of silicone with micron-scale shape fidelity. A hierarchically structured Schwarz-D membrane reactor was successfully fabricated that could survive fluid and gas flowing through the interpenetrating domains without leaks. The hierarchical structure aided in manifolding fluidic ports to the reactor for counter-current flow. The performance was promising for the geometries used, but the calculated volumetric mass transfer coefficients were lower than typical values for conventional monoethanolamine (MEA) solvent towers. Since the performance matched well with theoretical analysis of the membrane reactors, it was identified that the limiting factor of the reactor performance was due to the thickness silicone walls of the prototypes, where wall thicknesses less than 50 µm were necessary to achieve good mass transfer coefficients in a large-scale reactor design.

The second generation of reactor designs centered on using the TPMS geometries for structured packings in absorption towers. The current state of the art in absorption columns for CO_2 capture typically uses commercially available structured packings (e.g., Mellapak 250Y). The most common of these structures uses corrugated sheets of metal that are stacked in an alternating manner within an absorption tower. Liquid solvents and rich flue gas are flowed counter-currently in these towers, using the packings as a means of providing surface area for the two streams to react with each other. AM-based TPMS geometries have the advantage of improving the flow distributions, integrating multi-functional material features, and enhancing fluid mixing. A qualitative improvement of liquid distribution is shown in Figure 5.

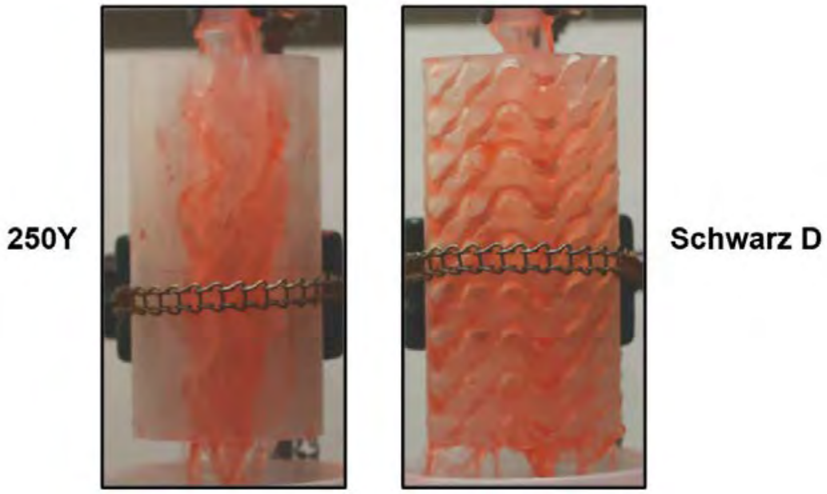


Figure 5: Fluid flow through conventional packing geometry (left) and TPMS packing geometry (right).

Alongside experimental measurements, computational mass transfer simulations were also explored. The model was incorporated into the open source computational fluid dynamics (CFD) package "OpenFOAM." The model couples the Volume of Fluid (VOF) method, which simulates the multi-phase gas and liquid flows, with an interfacial reactive mass transfer modeling procedure to incorporate reactive mass transport mechanism into the simulations. Using the simulations, a range of TPMS structures were explored for their potential use as structured packings. These results shown in Figure 6 indicate that the Schwarz-D geometry is predicted to have the best mass transport, followed by the $J_sI_{xxx}I_{zx}IP_2IZ$ structure. Quantitative metrices of fluid distribution and interfacial area based on experimental and computational modeling are shown in Figure 7.

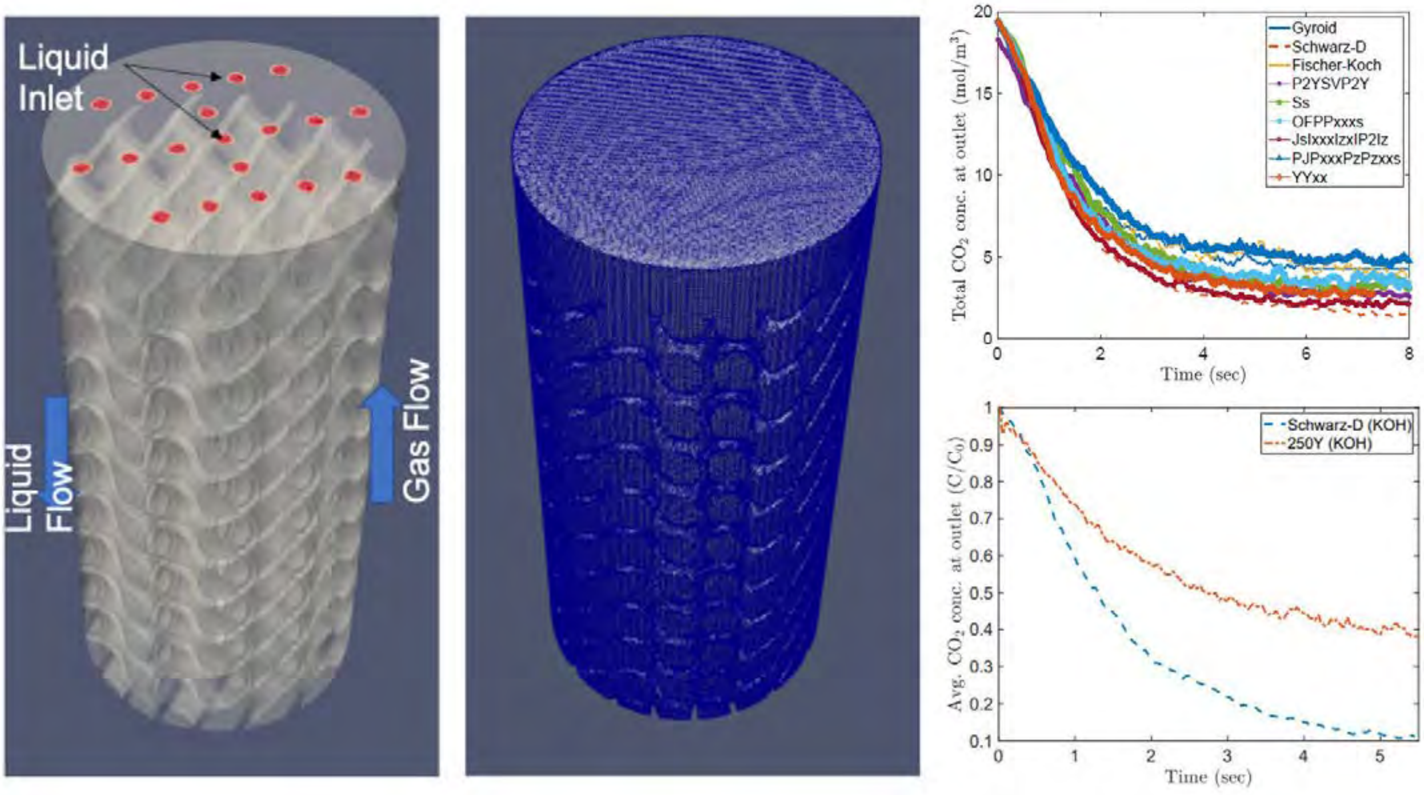


Figure 6: Computational modeling of TPMS-structured packings. Across a range of different TPMS geometries, the Schwarz-D structure resulted in the best capture performance.

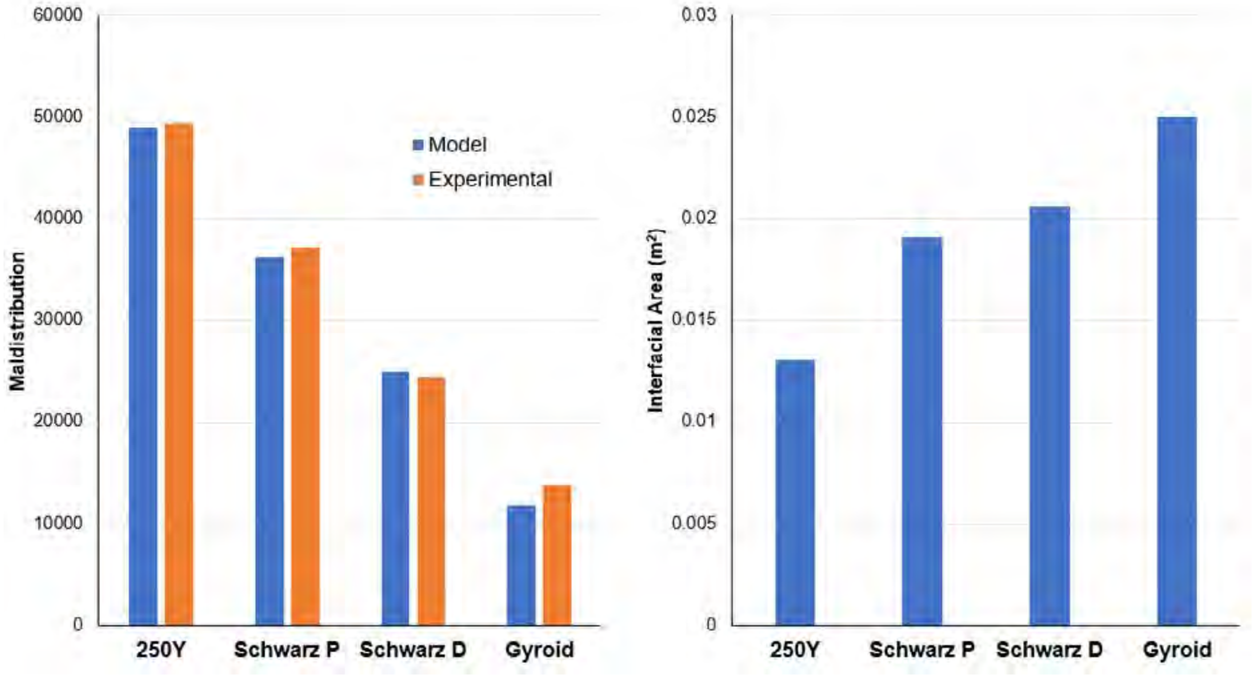


Figure 7: Liquid maldistribution and interfacial area of different geometries. TPMS structures all exhibit better liquid flow properties compared to conventional 250Y geometries.

To visually demonstrate the improved performance of the printed TPMS-structured packings compared to printed 250Y packing sections, a CO_2 capture experiment incorporating a pH-sensitive dye was performed. The partially transparent nature of the printed column allowed for facile visualization of the liquid flow and thus the time to color change, clearly indicating the difference in packing performance. The experiment utilized aqueous potassium carbonate (K_2CO_3) as a solvent with a pH-indicating dye. Figure 8 highlights the color change visualization and shows the pH change profiles of the two experiments, indicative of the effective solvent loading over time and thus the CO_2 removal rate. The more rapid pH change with Schwarz-D packings was attributed to improved mass transfer and effective interfacial area with identical nominal specific surface areas.

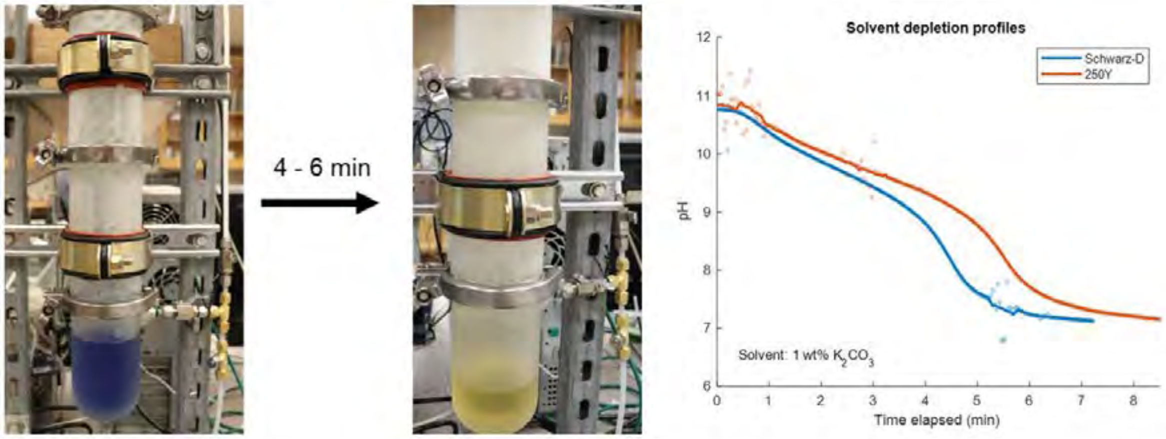
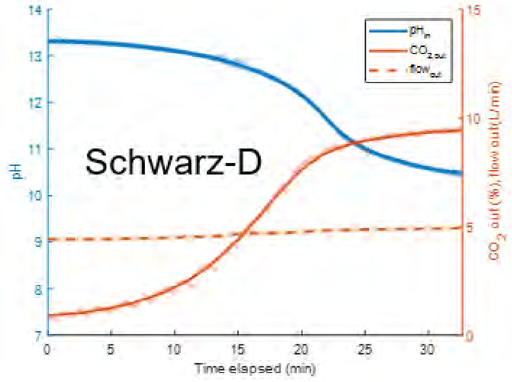


Figure 8: Colorimetric change of an aqueous K_2CO_3 solvent using thymol blue as an indicator dye. pH evolution profiles for two absorber experiments using a TPMS Schwarz-D geometry and a conventional 250Y geometry.

The Schwarz-D, Gyroid, and 250Y structures were quantitatively compared to each other using this method of measuring the depletion time of a solvent (Figure 9). Experiments were conducted using a reservoir of sodium hydroxide (NaOH) and 10% CO_2 in a counter-current flowing column. The solvent depletion time was then measured to determine the effects of the use of TPMS packings. Similar to the visual experiments with K_2CO_3, the hydroxide solutions also depleted faster in the TPMS geometries when compared to the 250Y structure. Furthermore, the Schwarz-D structure achieved a faster depletion than the gyroid structure.



Packing	Depletion time (pH < 11) [min]
Schwarz-D	25.0
Gyroid	27.8
250Y	32.6

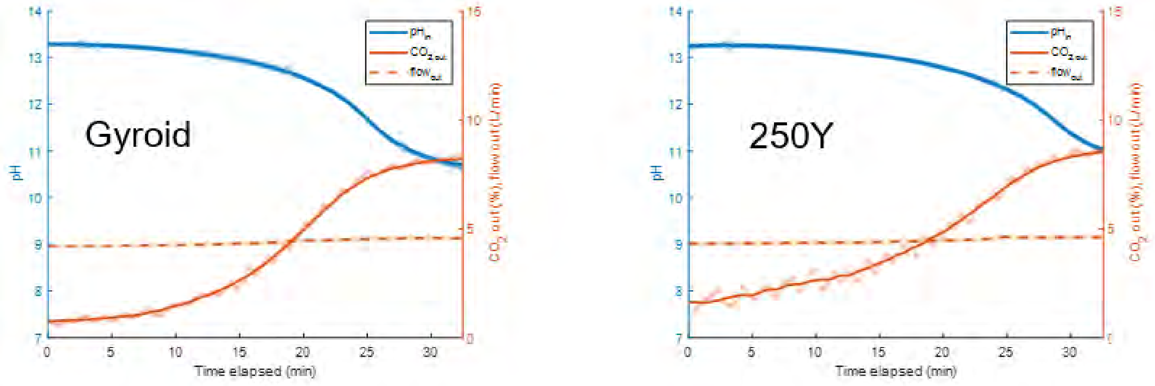


Figure 9: Relative comparisons of Schwarz-D, Gyroid, and 250Y structures. The Schwarz-D structure was found to be the best performing of the geometries.

The heat transfer performance of a set of TPMS and periodic nodal surface (PNS) structures were also evaluated by numerically computing the friction factors and Nusselt numbers in the laminar flow regime. In this evaluation, these structures were found to have higher friction factors when compared to straight channels, but also had higher Nusselt numbers. Furthermore, the Nusselt number enhancement improved with increasing Reynolds number. Among the TPMS geometries studied, the Schwarz-D had the best heat transfer performance while the Schwarz-P was the worst performing structure, as shown in Figure 10. No correlation between being a TPMS versus PNS and the associated heat transfer performance was found.

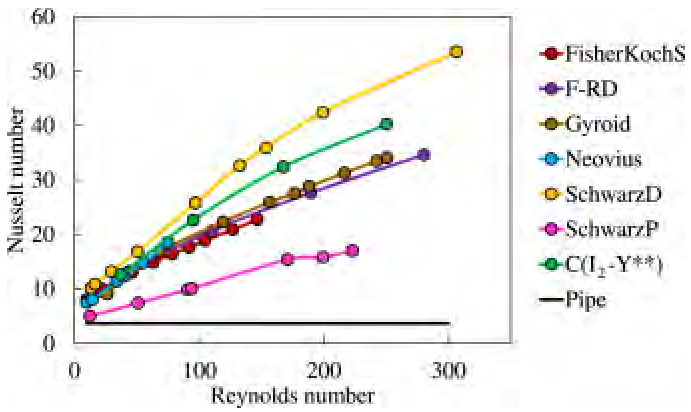


Figure 10: Nusselt numbers for the TPMS and PNS structures.

A rate-based model of an absorption column was also developed and used to analyze several intercooling strategies utilizing these "heat exchange packings." A number of optimal temperature profiles were calculated, which minimized the column height required to achieve a fixed degree of separation for a given set of gas and liquid inlet flow rates (Figure 11). While these optimal profiles may not be realized in an actual system, their calculation provides a base case that is useful when comparing different intercooling approaches and determining whether more advanced intercooling may be worthwhile. The optimal temperature at any point along the column represents a trade-off between lowering the temperature to increase the absorption driving force and increasing the temperature to increase absorption kinetics.

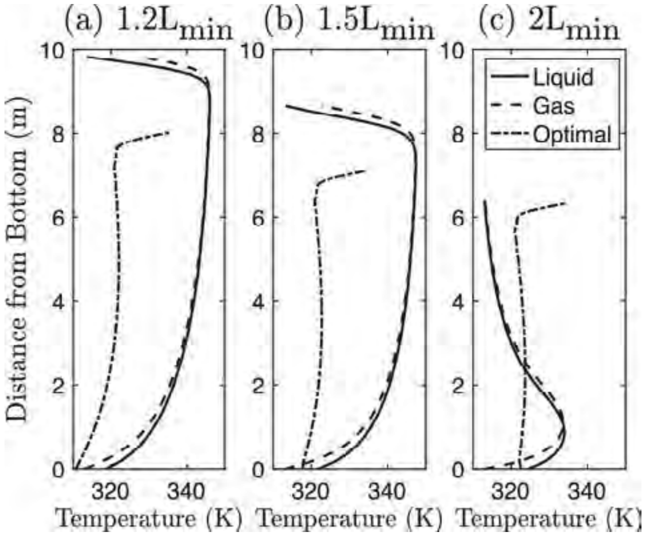


Figure 11: Optimal and adiabatic temperature profiles under conditions for (a) 1.2 L_{min}, (b) 1.5 L_{min}, and (c) 2 L_{min}.

technology advantages

- Novel reactor geometries enable absorbers and fixed beds with integrated heat exchange, membrane separators with minimal pressure drop, and high efficiency heat exchangers.
- TPMS packings are predicted to have better liquid distributions and liquid-gas interfacial area and enhance fluid mixing.
- Lower cost of plastic printed packings compared to stainless steel at bench-scales.

R&D challenges

- Optimizing geometry of TPMS for best performance at the process level.
- Identifying new material or fabrication strategy for TPMS membrane reactors.
- Part-scale fabrication using AM.

status

LLNL has concluded that for single-phase flow in membrane reactors, smaller feature sizes are better, to the limits of fabrication. Printed plastic packings using multiple materials were demonstrated. Hydrophobic surfaces in the stripper are promising for polarity-swing solvents. Kg-scale testing and kg-scale production was solved for larger-scale demonstrations. TPMS membrane reactors showed promise, but the fabrication process was limited by scalability. TPMS geometries exhibit high thermal transport properties within a wide range of geometries (the Schwarz-D structure demonstrated the best performance). LLNL developed an optimization framework for structured packings with integrated heat exchange. TPMS-structured packings exhibited improved liquid distributions and improved performance. Altogether, a 20–50% reduction in absorber capital cost may be possible with these TPMS packings; however, manufacturing costs at scale are uncertain.

available reports/technical papers/presentations

Nguyen, D., “High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing,” NETL Carbon Management and Oil and Gas Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Nguyen.pdf*

Stolaroff, J., “High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing,” BP2 Review / Project Continuation Meeting, Pittsburgh, PA, August 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11815&filename=High-Efficiency%2c+Integrated+Reactors+for+Sorbents%2c+Solvents+and+Membranes+Using+Additive+Manufacturing.pdf*.

Stolaroff, J., “High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Stolaroff%20-%20NETL%20Program%20Review%202019.pdf*

Stolaroff, J., “High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Stolaroff-LLNL-Reactor-Additive-Manufacturing.pdf*.

Stolaroff, J., “High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/1J-Stolaroff1-LLNL-High-Efficiency--Integrated-Reactors.pdf*.

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Nguyen, Du, Maxwell Murialdo, Katherine Hornbostel, Simon Pang, Congwang Ye, William Smith, Sarah Baker, William Bourcier, Jennifer Knipe, Roger Aines, and Joshuah Stolaroff. “3D Printed Polymer Composites for CO_2 Capture.” *Industrial & Engineering Chemistry Research* 58, no. 48 (December 4, 2019): 22015–20. *https://doi.org/10.1021/acs.iecr.9b04375*.

Y Fu, J Bao, C Wang, RK Singh, Z Xu, G Panagakos. CFD study of countercurrent flow in triply periodic minimal surfaces with CO_2BOL solvent. CCSI^2 Technical Report (2019) [with LLNL design files]

Advancing Post-Combustion CO_2 Capture Through Increased Mass Transfer and Lower Degradation

primary project goal

The University of Kentucky Center for Applied Energy Research's (UK CAER) project is developing three techniques to enable aqueous post-combustion carbon dioxide (CO_2) capture technologies to meet the U.S. Department of Energy (DOE) performance and cost targets of 90% CO_2 capture, 95% purity, at a cost of less than $30/tonne CO_2 captured. To reduce the cost of CO_2 capture, critical elements need to be addressed, including how to increase CO_2 mass transfer (reduce capital cost), how to reduce solvent makeup (lower the operational cost) resulting from degradation, and how to address the potential environmental issues (permitting hurdles) from nitrosamine formation. The specific objectives of this project are to develop a 3D-printed dynamic polarity packing material with increased turbulent liquid flow and controlled gas-liquid bubble formation to increase CO_2 mass transfer into amine solvents; investigate the impact of additives on the physical properties of solvents and their relationship to bubble formation to boost mass transfer while reducing aerosol formation; and decompose nitrosamines derived from amine solvents through development of an electrochemical treatment process. The project team is developing and fabricating customized dynamic packing using advanced manufacturing techniques, installing the packing into UK CAER's bench-scale (less than 0.1-megawatt-thermal [MWth]) CO_2 capture unit, and conducting parametric and long-term testing with additive-modified solvents. Additionally, an electrochemical cell with stationary carbon electrodes is being designed and evaluated for the adsorption and decomposition of nitrosamines from wash water solutions collected from UK CAER's 0.7-megawatt-electric (MWe) small pilot CO_2 capture system located at Kentucky Utilities' E.W. Brown Generating Station.

technical goals

- Develop a library of structure/property relationships that can be used as a guideline for choosing effective additives for a given solvent or blend.
- Design and fabricate dynamic polarity packing based on a range of solvent property parameters for a given liquid-gas ratio.
- Evaluate selected solvents in UK CAER's bench-scale CO_2 capture unit with conventional structured packing to serve as a baseline.
- Replace the conventional packing in the bench-scale unit with 3D-printed dynamic packing and test the selected solvents under the same operating conditions to determine mass transfer enhancement.
- Test selected solvent additives in the bench-scale unit to evaluate mass transfer enhancement and reduced energy demand.
- Evaluate the electrochemical cell using wash water collected at UK CAER's 0.7-MWe small pilot CO_2 capture system to measure the ability to maintain nitrosamine levels below 0.5 parts per million (ppm).
- Conduct parametric testing of the combined dynamic packing solvent/additive system and identify optimum operating conditions to achieve an increase in mass transfer.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Post-Combustion Power Generation PSC

key technology:

Novel Concepts

project focus:

Solvent Enabling Techniques for Coal-Based Flue Gas

participant:

University of Kentucky

project number:

FE0031661

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Jesse Thompson
University of Kentucky
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partners:

Lawrence Livermore National Laboratory

start date:

10.01.2018

percent complete:

85%

- Perform a long-term testing campaign under optimized operating conditions to evaluate the stability of dynamic packing and electrochemical cell and examine aerosol formation, corrosion, and solvent degradation.
- Perform a high-level techno-economic analysis (TEA) based on the collected bench-scale test data.

technical content

This UK CAER and Lawrence Livermore National Laboratory (LLNL) project involves the development and fabrication of customized 3D-printed dynamic packing to increase CO_2 mass transfer in the absorber column. UK CAER is designing, fabricating, and testing an electrochemical cell to adsorb and decompose nitrosamines from the water wash. After both systems have been constructed, they will be tested on UK CAER's bench-scale CO_2 capture unit. The specific activities in this project include: (1) quantifying the CO_2 mass transfer improvement from the customized 3D-printed dynamic polarity packing in the absorber by utilizing UK CAER's existing less-than-0.1-MWth, 3-inch ID CO_2 capture column; (2) quantifying the energy consumption savings associated with the mass transfer enhancement from the dynamic polarity packing; (3) conducting detailed studies to understand how the solvents' physical properties can be utilized to form controllable gas bubbles to boost the mass transfer area and impact wettability, degradation, and aerosol formation; (4) quantifying the benefits of UK CAER's electrochemical cell in regards to decomposing nitrosamines; and (5) collecting the necessary information/data to conduct a high-level TEA of the proposed technologies.

A systematic approach was taken to develop understanding of the structure/function relationships for additives in a rational series of amine solvents in terms of bubble formation, the stability of gas-liquid interface film, and solvent polarity. First, physical properties such as surface tension, viscosity, elasticity, and contact angle were measured in aqueous amine solvents with different pKa, polarity, and functional groups (i.e., –OH, -N, -R). Commercially available amines, including primary, secondary, and tertiary amines, as well as amines with different functional groups, were prepared and examined at various concentrations (e.g., 3–5 M) and at lean (~0.2 carbon/nitrogen ratio) and rich CO_2 loading (~0.4 carbon/nitrogen ratio). Water-soluble chemical additives were then selected with different functionality and chemical structures (surfactants, inorganic metal corrosion inhibitors, organic oxidation inhibitors, and metal-ligand CO_2 hydrolysis catalyst) and added to the amine solvents. The physical properties of the amine solvents with the additives were then measured at lean and rich CO_2 loading to assess how the additives changed the solvent physical properties. The main physical property modification came from addition of a surfactant, which resulted in a decrease in the surface tension of the solvent and a reduction in the contact angle relative to a hydrophobic surface, such as a polymeric material. The decrease in contact angle implied better wetting (coating) on the packing by the solvent, leading to better gas-liquid contact. This result has implications when considering the use of plastic 3D-printed packing material as a substitute for steel structure packing in the absorber column.

One important factor when exploring the use of polymer packing is the stability of the polymer when exposed to the caustic CO_2-loaded amine solution at elevated temperatures. The stability of the polymeric packing material after exposure to CO_2-loaded amine solvent at absorber temperature (60°C) was examined through an estimated 5,000 hours. Changes to mass, thickness, and contact angle versus water and the amine solvent were monitored every 1,000 hours. The results are shown in Figure 1. The three polymer materials examined showed minimal changes in mass, thickness, and contact angles versus both water and the CO_2-loaded amine solvent. Based on the amine stability studies, acrylonitrile butadiene styrene (ABS), nylon, and high-density (impact) polystyrene (HDPS) were shown to be stable upon exposure to CO_2-loaded amine solvent at anticipated absorber temperatures.

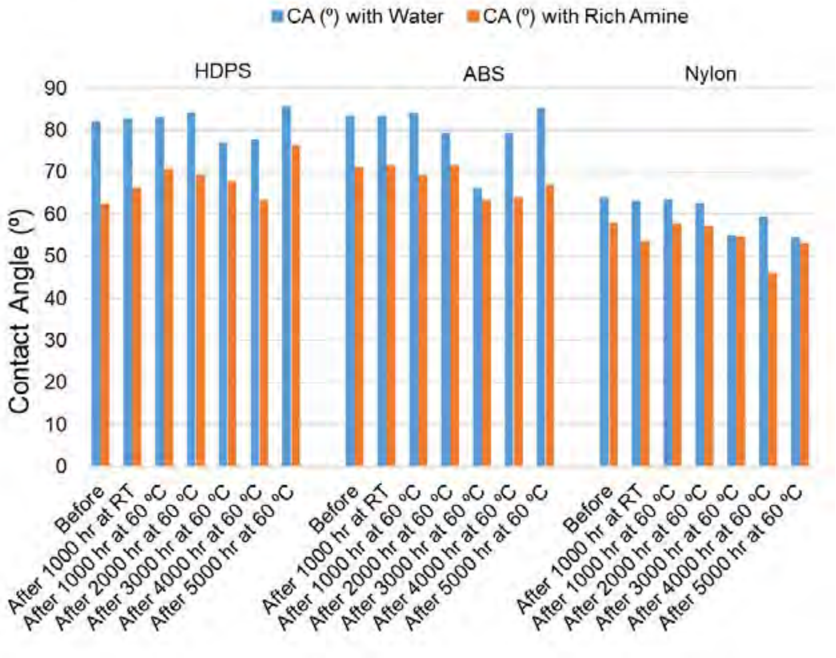

Figure 1: Contact angle (°) changes of polymeric materials after long-term exposure to CO_2-loaded amine solvent.

To compare the wettability of the polymer packing, polished coupons of the HDPS, ABS, nylon, and stainless steel (SS) were collected, and contact angles were measured with water and an amine solution (Figure 2). The contact angle (wettability) versus water of HDPS and ABS are similar, while nylon and SS are lower and closer to each other. All the packing materials showed a lower contact angle with the amine solvent compared to water. The contact angle of nylon was the closest to SS, with both ABS and HDPS having two to three times larger contact angles.

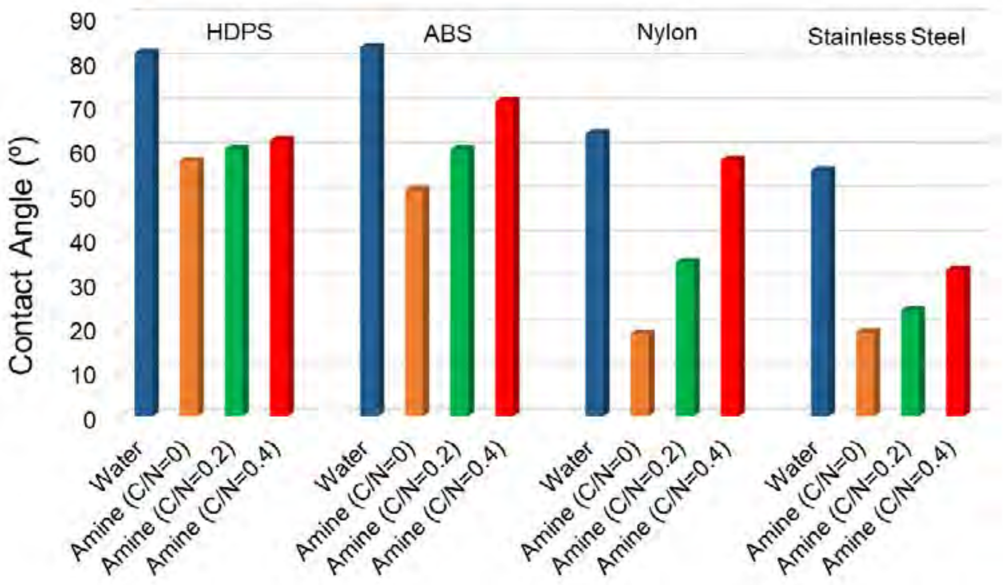

Figure 2: Contact angle of water and aqueous amines (at different CO_2 loadings) on different packing material surfaces.

Four different packings, including SS, ABS, nylon, and three dynamic packings (DPs), were prepared for testing in a small bench CO_2 capture unit (Figure 3). All of the 3D-printing packings are in 250Y shape to compare with regular steel packing. The DPs have an ABS external shell with nylon as the core material and co-printed with additional section of HDPS as the more hydrophobic material. DP-1 has a nylon base with a small amount of HDPS embedded in the packing interior with a staggered pattern; DP-2 has stacked alternating interior pattern with 50% HDPS and 50% nylon material; DP-3 also has a nylon base with a small amount of HDPS embedded in arrow patterns.

Figure 3: 250Y-type packing comparison with different dynamic design patterns (left to right) SS, DP-1, DP-2, DP-3.

The best performing polymer packing from a detailed parametric testing campaign was tested for long-term performance and stability. The long-term packing verification test included 500 hours of stable CO_2 capture under optimal conditions. The polymer packing shows a consistent improvement in mass transfer, leading to an average relative 15.9% improvement in CO_2 absorption and 19.7% decrease in energy consumption compared to the baseline Mellpak 250Y SS packing (Figure 4).

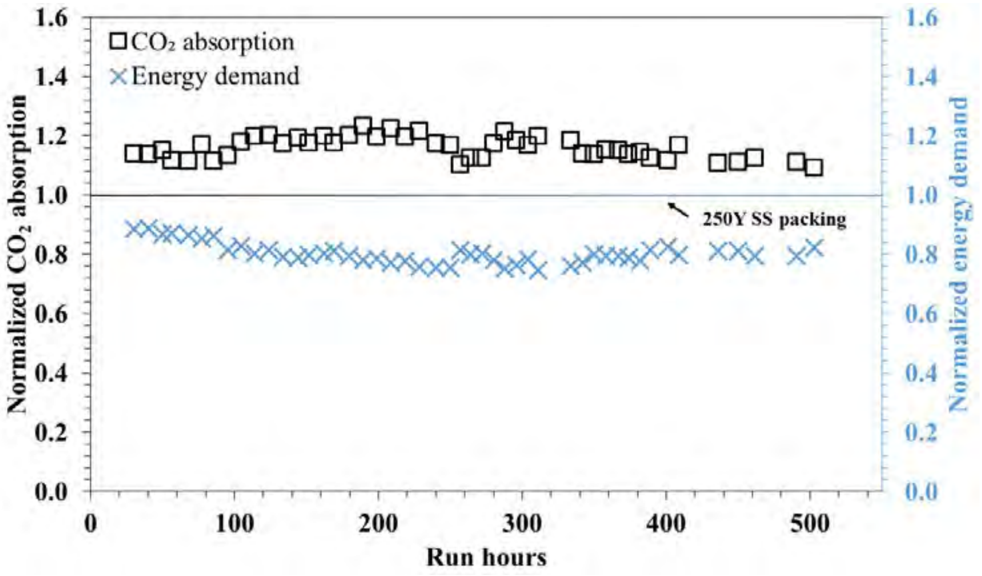

Figure 4: CO_2 absorption efficiency and energy demand during the 500-hour long-term testing.

To address the potential environmental concerns associated with nitrosamine formation in CO_2 capture systems, an electrochemical treatment cell is being developed to destruct nitrosamines from the absorber water wash. The electrochemical cell is being evaluated using wash water solutions collected at UK CAER's 0.7-MWe small pilot CO_2 capture system. The liquid under investigation represents the actual composition of wash water from an operating pilot CO_2 capture system that treats coal flue gas. A preliminary design of a flow-through electrochemical cell with carbon xerogel (CX) electrodes was generated (Figure 5, top) and fabrication has been completed. Recent testing demonstrated the ability to continuously reduce at least 85% of the nitrosamines present in the water wash with an efficiency above 15%, well above the original target values.

Using the knowledge learned during flow-through electrochemical cell (e-cell) experiments with the CX electrodes, where variable solution flow rates, currents, and nitrosamine concentrations were evaluated, nitrosamine removal and efficiency was optimized. A simulated water wash solution was spiked with concentrated nitrosamines to create nitrosamine concentrations of approximately 50 ppm N-Nitrosopyrrolidine (NPY), N-Nitrosodiethylamine (NDEA), and N-Nitrosomorpholine (NMOR), for a total of around 150 ppm. The spiked solution flowed through the e-cell for 12 hours with a 25-mA charge. The removal behavior of NPY, NDEA, and NMOR during the 12-hour electrolysis period are shown in Figure 5 (bottom). The concentrations of all three nitrosamines reached the limit of detection (LOD) within 12 hours and were removed with a 99% removal efficiency. The total charge efficiency during the 12-hour electrolysis period was calculated with an average efficiency of 33% during this time.

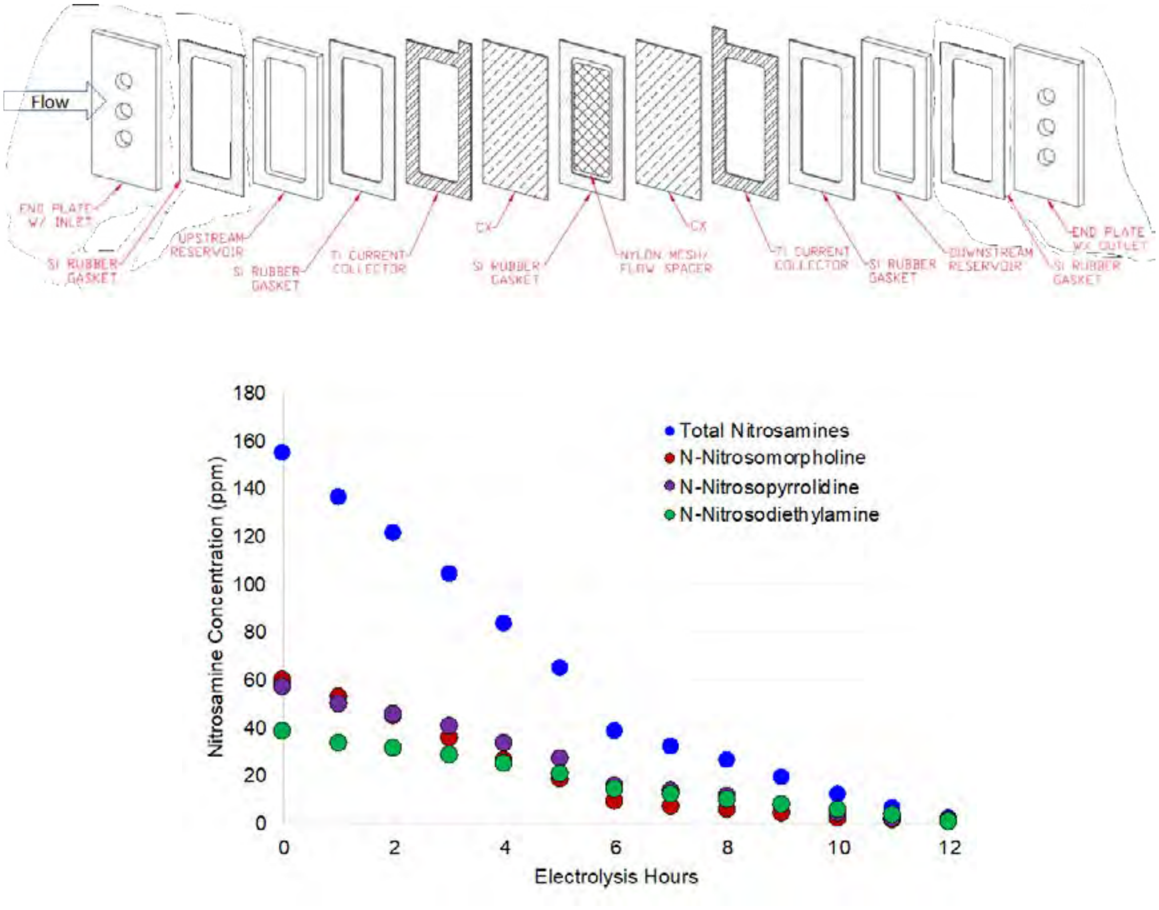

Figure 5: Flow-through e-cell schematic with CX electrodes (top) and nitrosamine destruction to below detection limit within 12 hours of electrolysis (bottom).

The TEA completed as part of this study compared various CO_2 capture solvent configurations. The most promising results are shown in Table 1.

TABLE 1: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	\$34.47	\$30
Cost of Carbon Avoided	\$/tonne CO_2	\$51.88	\$45
Capital Expenditures	\$/MWhr	\$42.11	\$40
Operating Expenditures	\$/MWhr	\$51.09	\$45
Cost of Electricity	\$/MWhr	\$93.20	\$80

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

technology advantages

- Increased CO_2 mass transfer and lower solvent regeneration energy.
- Enhanced CO_2 absorption rate reduces absorber size, lowering capital and operating costs.
- Use of solvent additives increases solvent wetting on packing.
- Electrochemical treatment process addresses environmental concerns at high selectivity with very low operational cost.
- Technology can extend over a broad spectrum of CO_2 capture systems, including many solvent-based systems.

R&D challenges

- Compatibility of packing material with actual flue gas and solvent impurity.
- Foaming with additives in long-term operation.

status

All Budget Period 1 tasks have been completed. Packing material and enhanced solvent have completed a long-term test and a high-level TEA is currently underway.

available reports/technical papers/presentations

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Electrochemically-Mediated Amine Regeneration in CO_2 Scrubbing Processes

primary project goal

The Massachusetts Institute of Technology (MIT) advanced a novel carbon dioxide (CO_2) capture technology using traditional amine-based solvents, but with the key innovation of using electrochemical regeneration of the solvent instead of conventional thermal regeneration. By utilizing cost-effective reduction/oxidation of metal ions to electrochemically enable the capture and release of CO_2 by traditional amine sorbents and thereby eliminating the demand for steam characteristic of conventional amine regeneration technology, the parasitic power requirement for operating the process was markedly less than that of conventional methods. This enabled substantial savings in the cost of electricity (COE) for carbon capture process scenarios, with promise to meet programmatic U.S. Department of Energy (DOE) carbon capture goals.

technical goals

- Develop an optimized electrochemical cell configuration/design and size, allowing best efficiency and cost performance for scalable carbon capture processes for commercial-scale coal-fired plants.
- Validate system using electrochemically mediated amine regeneration in a CO_2 scrubbing cycle for capture of at least 90% of CO_2 from coal-derived flue gas while demonstrating significant progress toward achievement of the DOE target of less than 35% increase in levelized COE (less than \$40/tonne CO_2).
- Reduce energy requirements 20–40% relative to that of baseline monoethanolamine (MEA) capture. Achieve specific regeneration energy of 0.91 gigajoules (GJ)/tonne CO_2.
- Demonstrate electrochemical cell stability over 15 days continuous operation, at simulated flue gas flow rate enabling capture of 0.01 kg CO_2 per day.

technical content

MIT termed their technology as Electrochemically Mediated Amine Regeneration (EMAR). In conventional amine regeneration-based capture processes, a standard amine solvent such as MEA is contacted in countercurrent flow with CO_2-containing flue gas in an absorption column at relatively low temperature (less than 60°C). At lower temperatures, CO_2 readily reacts with the amine forming an amine-CO_2 complex, and given suitable contact time and solvent flow in the absorption column, high levels of CO_2 removal (greater than 90%) can be attained. The rich amine solvent (containing elevated levels of absorbed CO_2) exiting the absorber column is preheated in a countercurrent heat exchanger and introduced into the desorber column, where it is further heated with low-pressure steam withdrawn from the power plant's steam cycle, to reach temperatures greater than 110°C. At elevated temperatures, the CO_2 is released from the solvent as a relatively pure stream of CO_2 that can be recovered. Hot lean solvent is cooled and returned to the absorption column. This conventional thermal regeneration-based process is depicted in the top half of Figure 1.

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Electrochemical Regeneration of Amine Solvents

participant:

Massachusetts Institute of Technology

project number:

FE0026489

predecessor projects:

N/A

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David Lang
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partners:

N/A

start date:

08.01.2017

percent complete:

100%

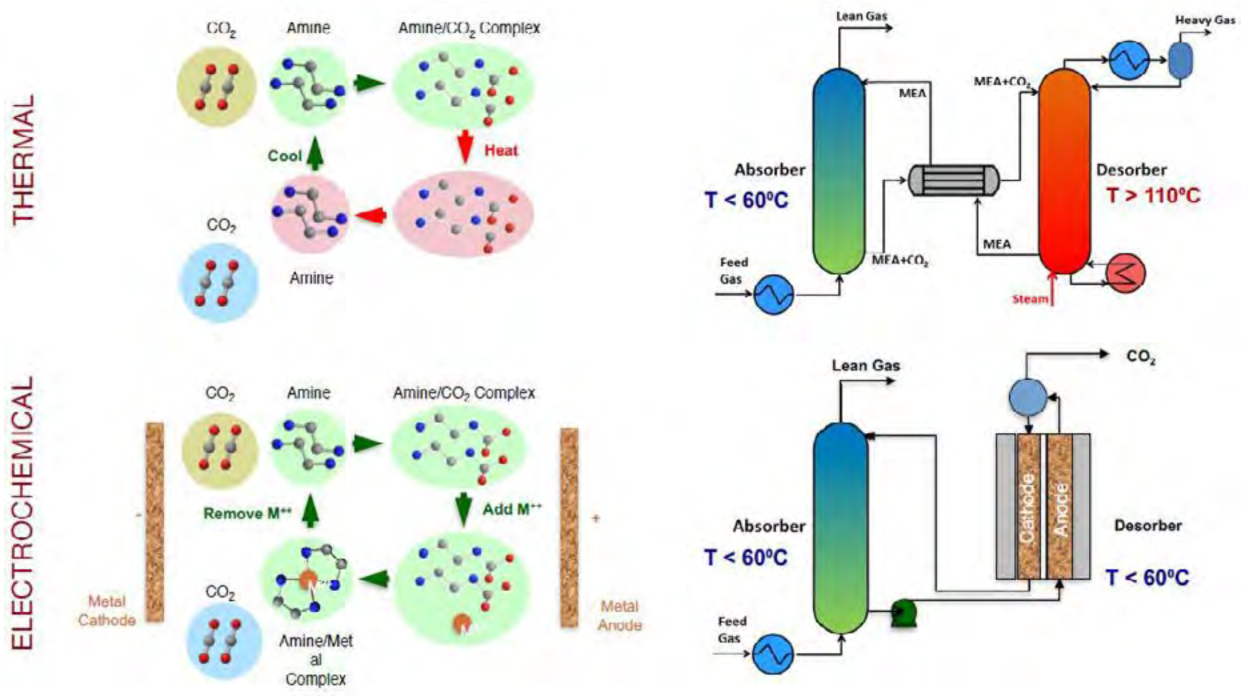

Figure 1: Electrochemically mediated versus thermal amine regeneration.

In EMAR (depicted in the bottom half of Figure 1), the process used the same type of absorption column and operating conditions therein. However, the rest of the process was significantly different. Instead of regenerating the rich solvent by increasing its temperature, the solvent passed sequentially through the anodic and cathodic sides of an electrochemical cell. On the anodic side, certain metal ions enter solution and react with the amine/CO_2 complexes in the rich solvent. If the metal ions have sufficiently strong binding with the amines, they displace the CO_2 and cause it to be liberated in pure gaseous form, enabling its separation. On the cathodic side, the amine metal compound remaining behind is stripped of the metal ions, resulting in lean amine solvent ready to return to the absorber. Temperature remains essentially constant throughout the process, eliminating heat exchange operations and their associated energy losses and capital costs.

Because the EMAR process requires only a limited amount of electrical power to operate the electrochemical processes in the cells, it avoids the need to use steam withdrawn from the power plant's steam cycle, minimizing parasitic energy consumption. This is depicted in Figure 2, which compares the amounts of CO_2 capture work (units of kilojoule [kJ_e]/mol CO_2 captured) associated with the EMAR system, and those of comparative thermal amine systems. Note the EMAR system advantage in respect of steam withdrawals.

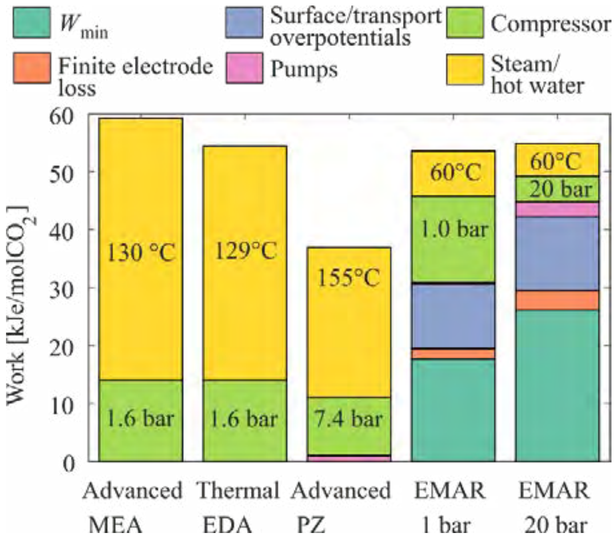

Figure 2: Comparison of capture work of thermal amine systems and EMAR systems.

This process concept has been proven at lab-scale, and ongoing work has been refining/optimizing the technology in terms of optimal selection of amine and metal ions, improving electrochemical kinetics, and optimizing cell design, as discussed below.

Amine Selection—Binding energies of metal ions with amines are specific to the amine. The binding energies must be strong enough to overcome the amine/CO_2 complexation, but higher binding energies demand high power consumption in the electrochemical cell to remove metal ions from the amine/metal complexes. Therefore, amine selection is important in optimizing the process. Adequate amine stability in the process is required. Candidate amines evaluated have included the following:

- MEA
- Diethanolamine (DEA)
- Diethylenetriamine (DETA)
- 2-Amino-2-methyl-1-propanol (AMP)
- Ethylenediamine (EDA)
- Pentamethyldiethylenetriamine (PMDTA)
- Aminoethylethanolamine (AEEA)
- Triethylenetetramine (TETA)
- Piperazine (PZ)

Metal Ions—Ion species, including Co^{2+}, Fe^{3+}, Fe^{2+}, Cr^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}, have been evaluated as possibilities for the optimal choice for metal/amine complex according to the following essential criteria:

- No precipitation in alkaline solvent.
- Redox active on metal electrode.
- Stability.

Screening of amine/metal complexes considering the candidates above has been performed. The screening methodology considered metal/amine stability in EMAR operating conditions, measurement of CO_2 capacity, testing of electrochemical reversibility, and validation of the CO_2 separation via electrolysis in batch reactors. Via the stability measurement, MIT concluded that only copper (Cu), zinc (Zn), and nickel (Ni) are plausible candidates to form metal-ligand complexes using off-the-shelf aqueous amine solvents. Nevertheless, only Cu-EDA can be modulated with electrochemical methods without incurring hydrogen evolution (i.e., water splitting). Therefore, MIT concluded that Cu-EDA is the most suitable candidate to be integrated into the envisioned EMAR process.

Electrochemical Kinetics—Rapid reaction rates of the complexes in the electrochemical cells are needed to accommodate the high solvent throughputs typical of large-scale post-combustion capture process scenarios. The EMAR cathode ideally operates in the absence of CO_2, but in practice CO_2 is present and tends to hinder the kinetics. Chlorides in solution have been found to improve performance significantly.

MIT investigated the thermodynamic potential of Cu-EDA and provided detailed speciation modeling of the Cu-EDA-water (H_2O) electrolyte. Results are informing modeling of the EMAR process, which will enable estimates of the energy consumption of an EMAR process in context of a post-combustion carbon capture cycle. The kinetics of the electrochemical reactions have been examined via deposition and dissolution experiments performed with rotating disk electrodes. The cathodic deposition of Cu is the slower process of the two Faradaic reactions and would require higher overpotential to drive out the desired reaction rate (i.e., current density). Suitable electrolyte combinations (with supporting salt) to decrease ohmic resistances and to minimize unwanted reactions have been identified. Both the Cu-EDA-H_2O-sodium (Na)-sulfate (SO_4) and Cu-EDA-H_2O-Na-chloride (Cl) systems were identified as stable electrolyte formulations. These electrolyte combinations have been further implemented in a bulk electrolysis setup that validates the electrochemical-thermal separation of CO_2. Results from systematic study and experimental validation of the CO_2 solubility constants have aided ongoing revision/improvement of the proposed thermodynamic cycle.

Cell Design—Ongoing work is optimizing cell architectures for fluid flow configuration and operational efficiency. Because CO_2 bubbles are formed in the cells, the design needs to efficiently accommodate removal of the gas. Prototype architectures are being developed for continuous CO_2 gas removal by utilizing gas/liquid separation membranes. In addition, cell stacking strategies to optimize volumetric efficiency and fluid flow will be investigated. Figure 3 gives an idea of the present configuration of cell engineering, showing metallic electrodes, channels, seals, etc. Figure 4 depicts a cell stacking concept.

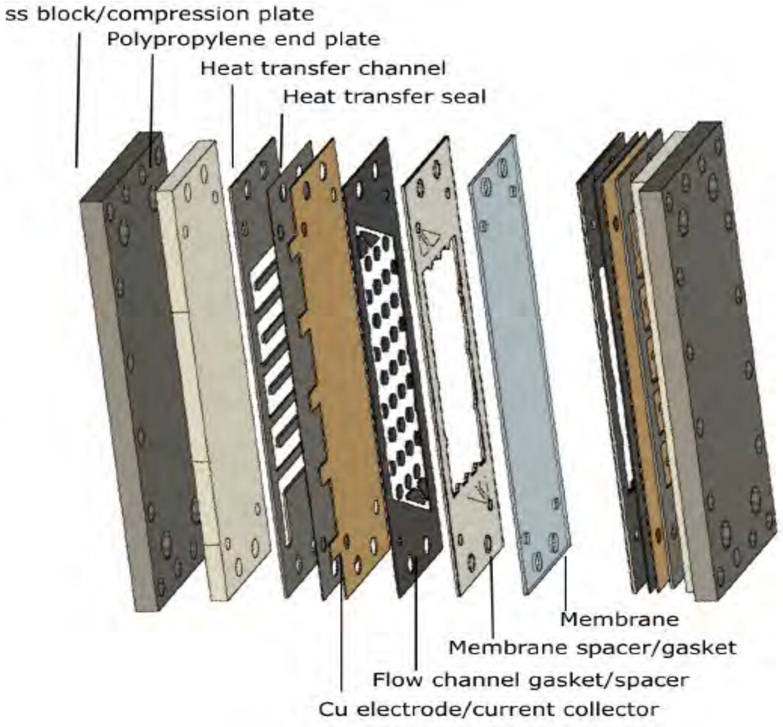

Figure 3: Electrochemical single-cell engineering.

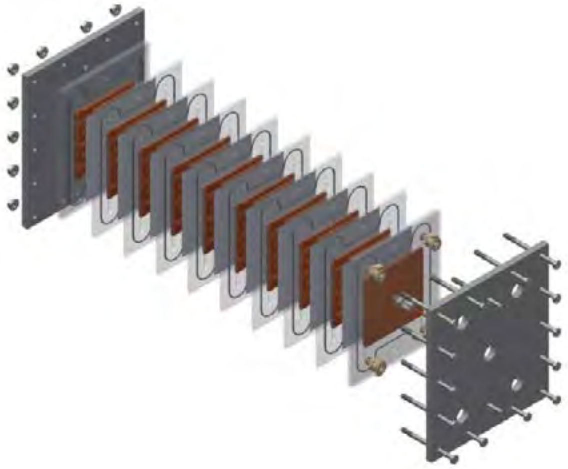

Figure 4: Cell stacking.

Process and Costs—MIT has created a process model accounting for all process unit operations (e.g., absorbers, heat exchangers, compressors), as well as additional energy efficiency losses (e.g., kinetic overpotentials) associated with an EMAR system in a full-scale power plant context. Figure 5 depicts the flowsheet for this model.

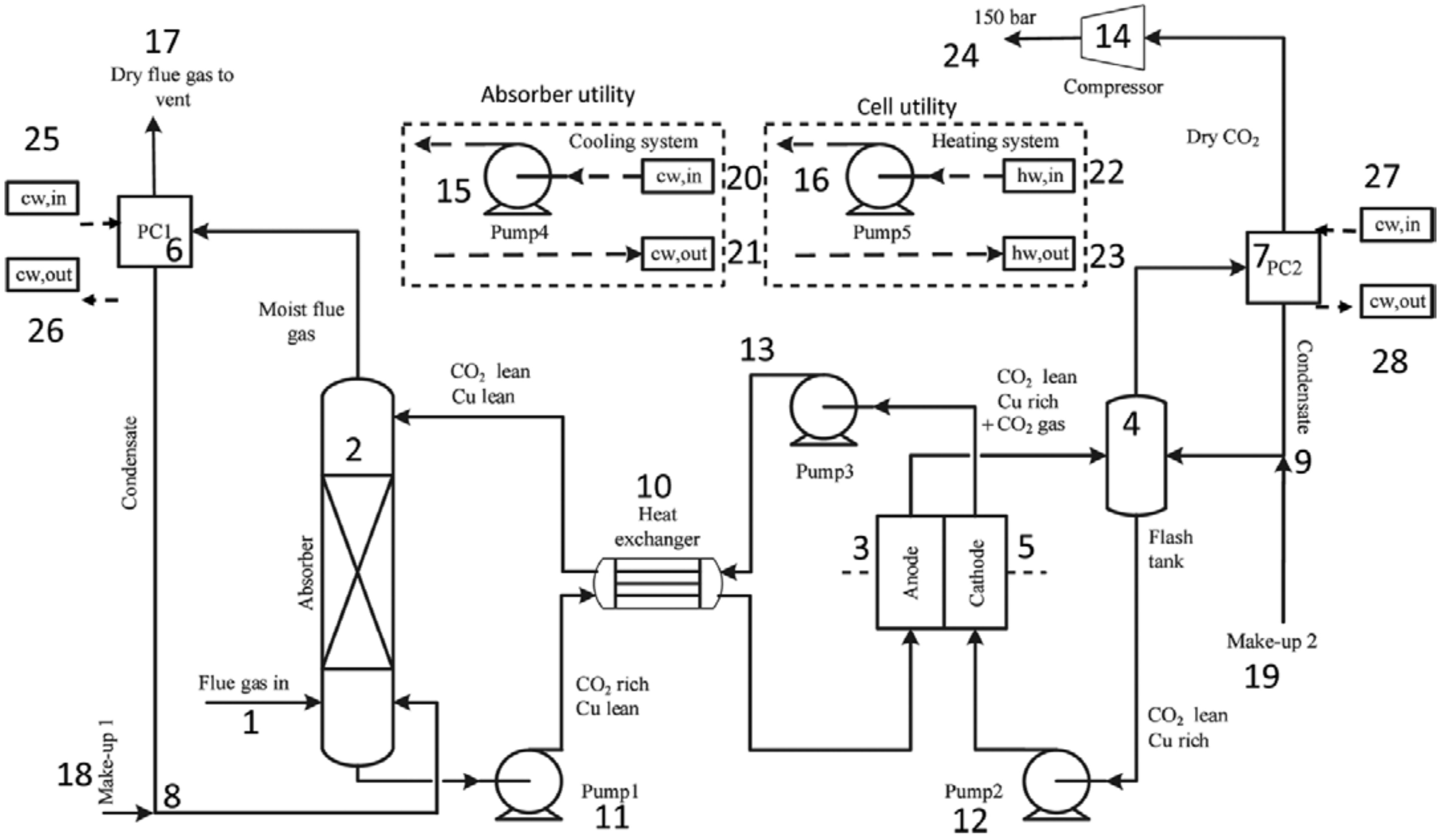

Figure 5: Detailed flowsheet simulated for EMAR process for carbon capture. Heat exchanger (#10) included for cases where heat recovery is necessary when desorption temperature is high in the stripping section. 1: flue gas source; 2: absorber; 3: anode; 4: flash tank; 5: cathode; 6 and 7: partial condenser; 8 and 9: mixers; 10: heat exchanger;11–13: pump; 14: compressor; 15 and 16: utility pump; 17: flue gas vent; 18 and 19: makeup streams; 20, 21, and 25–28: cold water source and sink; 22 and 23: hot water source and sink; and 24: compressed CO_2. (Int. J. Greenhouse Gas Control 2019, 82, 48–58)

A range of operating conditions and operation schemes were varied parametrically to identify reasonable overall energetics in the EMAR system process. Interesting findings of the process simulations include the realization that net energy demands can be significantly reduced if waste heat is available at temperatures below 90°C, and that the EMAR process is able to desorb CO_2 at pressures up to 20 bar with negligible additional energy penalty. Preliminary cost analysis of a full-scale EMAR process indicates a cost of around $60 per tonne of CO_2 avoided ($40 per tonne of CO_2 captured) in capture from post-combustion flue gas from a 550-megawatt (MW) coal-fired power plant. It is postulated that further reduction in cost should emerge from advanced process design, process optimization, and improved solvent formulation.

MIT has preliminary estimates of capital and operating costs of an EMAR system, as well as comparisons to baselines. Figure 6 shows the expected breakdown of equipment costs and offers COE comparisons to a no-capture case and conventional amine-based capture cases.

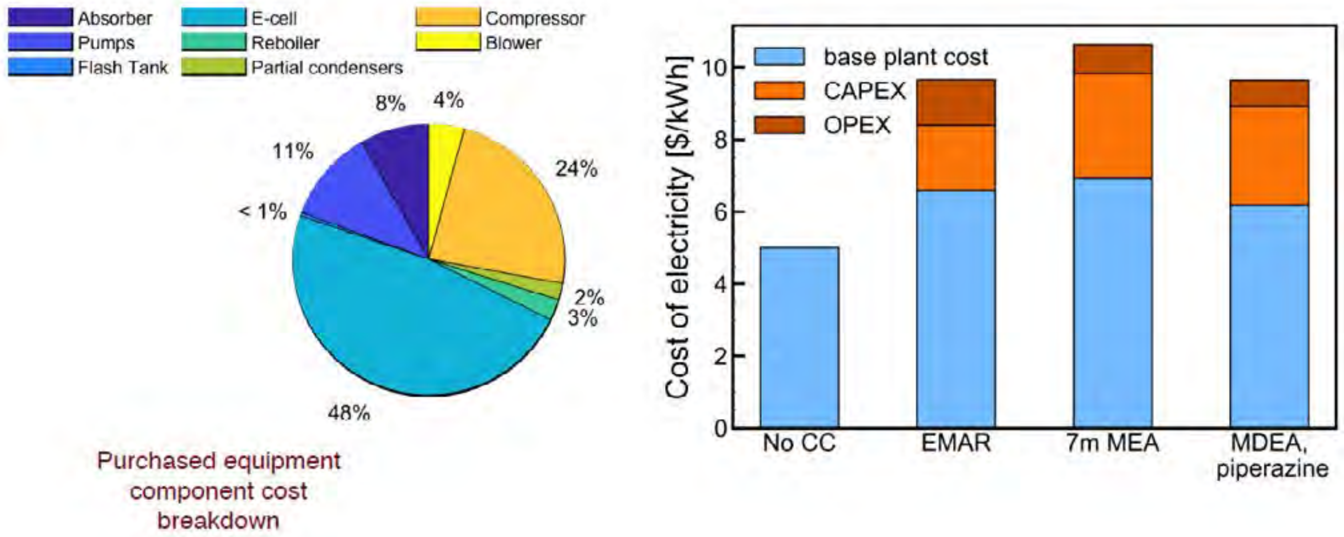

Figure 6: Capital cost breakdown and COE estimates/comparisons.

technology advantages

- Amine scrubbing with electrochemically mediated amine regeneration offers a combination of fast kinetics, low parasitic energy requirements, and process flexibility.
- Carbon dioxide gas recovered from the regenerator was at elevated pressure (up to 20 bar), lessening downstream compression requirements and saving energy.
- The process optimally operated at a regeneration capacity between 0.5–0.8 mol-CO_2/mol-amine.
- At a membrane unit price of less than $\$10/m^2$, the CO_2 capture cost may be reduced to below $\$50/tCO_2$ with optimized process conditions (e.g., desorption pressure and utilization of waste heat).
- Techno-economic analysis (TEA) indicated that the electrochemically mediated capture technology could have a significant economic advantage over state-of-the-art thermal amine processes, cutting capture costs by 30–60%.

R&D challenges

- Possible sensitivity of the process to disturbances and long-term operation viability. Since the system needed to switch the polarity of the electrodes and the corresponding process stream, this required implementation of an automation system that can accomplish both tasks for long-term operation stability.
- Validation of the basis for scale-up of the process to commercial-scale capability.
- Cell fluid flow channeling was a problem. Gas trapping in the fluid channel will reduce effective ionic conductivity, leading to reduced CO_2 separation. High velocities of liquid on the surface of the electrode will need to be ensured to minimize boundary layer thickness.
- Surfactants were evaluated to reduce CO_2 bubble size and minimize copper precipitation from electrodes.

status

MIT's electrochemically mediated amine regeneration technology has been previously developed from concept to a proof-of-concept lab-scale device, validating the feasibility and potential of the approach. Additional lab-scale work has been completed to further optimize the performance of the technology, with a Cu-EDA amine/metal complex identified as needed. Cell architecture, cell operation and kinetics, and process optimization were investigated. This study conclusively demonstrated the advantages of the EMAR process relative to conventional amine-based thermal swing capture processes. The EMAR process does not rely on steam integration, which leads to a more easily deployed system for a range of CO_2 capture applications.

available reports/technical papers/presentations

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Molecular Refinement of Transformational Solvents for CO_2 Separations

primary project goal

Pacific Northwest National Laboratory (PNNL) aimed to perform molecular refinement of third-generation water-lean solvents during this project. The objectives were to reduce volatility while retaining desirable physical and thermodynamic properties, study the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation), design new molecules that are resistant to these chemical degradations, and decrease infrastructure capital expenditures (CAPEX) while increasing longevity by replacing steel with cheaper and more durable plastics. The proposal was built on PNNL's integrated solvent development approach, with an integrated effort combining the elements of computation, advanced synthesis and testing capabilities, and comprehensive material property testing to refine advanced solvent performance while also reducing the CAPEX of these third-generation solvents.

technical goals

- Refine third-generation carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) solvents (aminopyridines [APs], diamines [DAs]) to reduce volatility while retaining favorable viscosity and CO_2 bonding enthalpy.
- Learn the molecular underpinnings of chemical degradation and develop strategies to mitigate or remove solvent decomposition with flue gas impurities, such as sulfur oxides (SO_X), nitrogen oxides (NO_X), oxygen (O_2), and hydrolysis.
- Measure the contact angles of water-lean solvents at varied CO_2 and water loadings on plastic surfaces and assess whether plastic infrastructure could be used in place of steel.
- Assess the reduction in CAPEX by substituting steels with fiber-reinforced plastic to determine progress toward the $30/tonne CO_2 target.
- Disseminate all findings to the U.S. Department of Energy (DOE), Carbon Capture Simulation for Industry Impact (CCSI^2), and peer-reviewed publications.

technical content

The PNNL team aimed to refine the secondary and tertiary properties that are limiting for water-lean CO_2BOL solvents. It was anticipated that the vapor pressure of third-generation solvents, such as APs or DAs, would be reduced to sub-parts-per-million (ppm) levels, effectively negating evaporative losses of solvent. PNNL expected to learn the reaction mechanisms of chemical degradations of carbamate and alkylcarbonate solvent molecules and learn how to redesign new molecules that are resistant to oxidation, nitration, and hydrolysis. PNNL aimed to demonstrate that new formulations exhibit an increase in solvent lifetime by two to four times. PNNL also expected that water-lean solvents under operating conditions (approximately less than 10 wt% water, 40°C, 0–50 mol% CO_2 loading) would be able to adequately wet plastics, enabling the substitution of cheaper and more chemically durable plastic to be used in place of steel. The removal of steel will effectively cease

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Molecular Refinement of (CO_2)-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-72396

predecessor project:
FWP-65872

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partners:
N/A

start date:
05.01.2018

percent complete:
100%

corrosion, improving solvent lifetime while negating the need for costly corrosion inhibitors. The substitution for fiber-reinforced plastics like polyethylene or polypropylene are estimated to provide an estimated 50% reduction in CAPEX for absorbers, strippers, and piping. These cost reductions are anticipated to help reduce CAPEX of carbon capture and storage (CCS) to enable third-generation solvents to meet DOE's prior $40/tonne cost metric, with the potential to achieve the revised $30/tonne metric.

PNNL was tasked with resolving three key problems associated with aminosilicone solvents: (1) susceptibility to disproportionation and hydrolysis; (2) significantly high CO_2-rich viscosity of the solvents; and (3) the need for co-solvent, thereby leading to increased capital and operational costs. To address all these challenges, the team has been working toward developing a novel DA-based system. In order to overcome the hydrolysis and disproportionation issues related to amino silicones, the silicone moiety was replaced with alkyl chains; however, these solvents solidified upon standing when CO_2 was loaded. It was hypothesized that two secondary amines were providing too much hydrogen bonding, so tertiary amine moieties were incorporated to reduce viscosity and solidification. The team started by designing a library for secondary/tertiary amines. The challenge was to down-select hundreds of molecules to a few candidate derivatives that would have a low viscosity. PNNL applied its previously developed reduced-order model to a library (Figure 1) to down-select to final derivatives. Their CO_2 uptake capacities were also evaluated. Several other analogues of DAs are in the process of being synthesized, as shown in Figure 1 (in the pipeline), in order to fully develop the structure activity relationship.

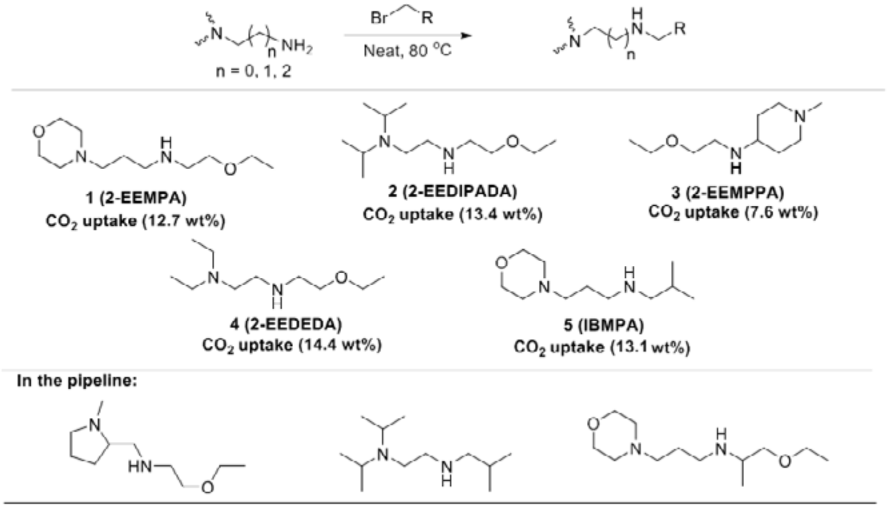


Figure 1: Selected library for non-volatile, low-viscosity secondary/tertiary diamines.

In order to address the volatility issue associated with the second-generation aminopyridine class of CO_2 capture solvents, two low-vapor pressure derivatives were prepared from modeling efforts to synthesize. These third-generation APs were functionalized with ether and morpholine motifs to promote high internal hydrogen bonding, but to also reduce vapor pressure. The synthetic approach for these two derivatives involved the condensation of 2-pyridinecarboxaldehyde with the corresponding amines to in situ generate imines, which were reduced by the treatment with sodium borohydride to yield 8a 3-methoxy-N- (pyridin-2-ylmethyl)propan-1-amine and 8b 2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine in 70% and 68% yields, respectively (Figure 2).

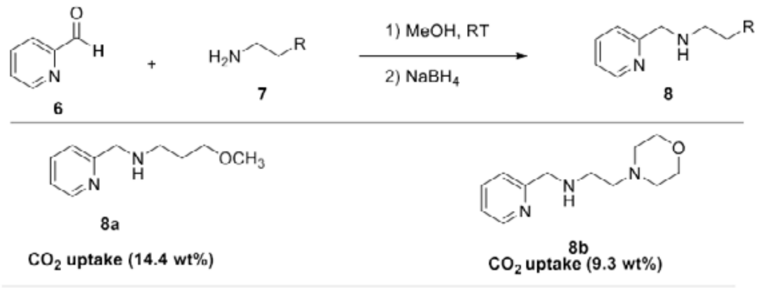


Figure 2: Synthetic methodology for the synthesis of third-generation aminopyridine derivatives.

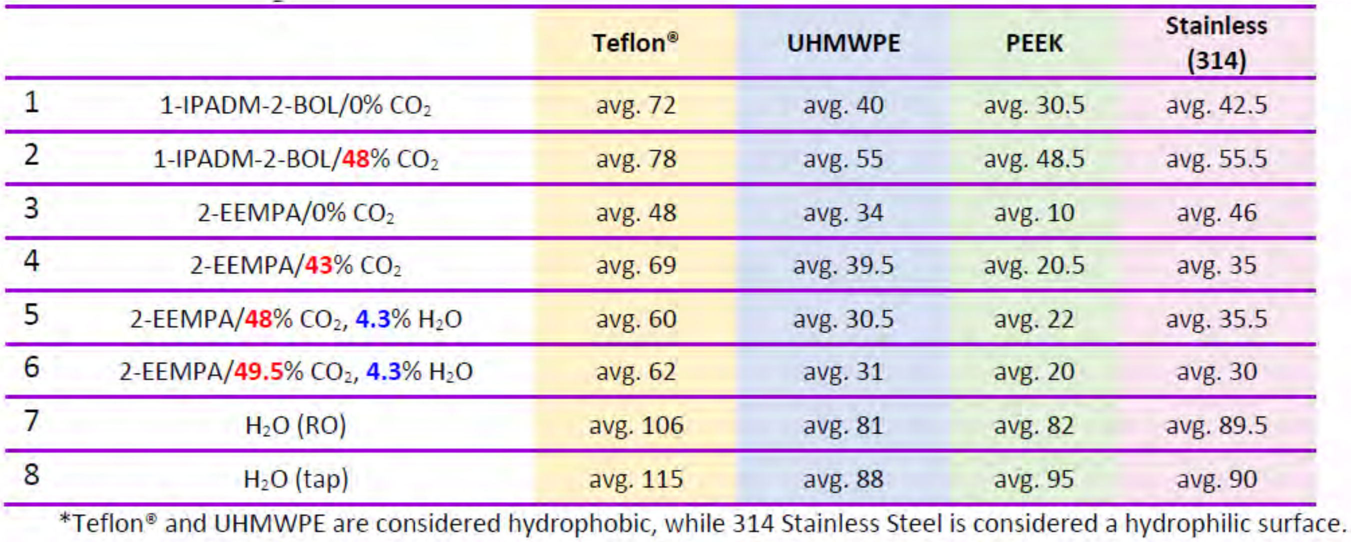
Once the AP and DA screenings were completed, the synthesis team started designing synthesis routes and began synthesis of the viable derivatives for comprehensive material property testing. For the testing, 50 grams (g) of the candidate derivatives were synthesized, and their physical and thermodynamic properties were evaluated using the in-house built pressure-volume-temperature (PVT) cell. Based on the results, PNNL recommends further testing on 8a as the final candidate AP for larger-scale testing, as it is cheaper, has lower molecular weight while having a lower CO_2-rich viscosity, and has stronger CO_2 sorption as compared to other AP derivatives. PNNL recommends 2-EEDEDA as the final DA candidate, as it has a low molecular weight and comparable CO_2 sorption as compared to other DA derivatives, while also having the lowest CO_2-rich viscosity (29 cP) of any known water-lean solvent ever developed.

PNNL performed large-scale molecular simulations to assess wetting properties and surface energies of a representative CO_2BOL alkanolguanidine (1-IPADM-2-BOL) adhered to 316 stainless steel and polyethylene interfaces. The goal was to determine what molecular-level interactions occur on either interface to determine how organics can wet stainless steel almost as well as plastic. Further, a second goal was to determine any reactions between the solvent molecules and the interface, to provide a better understanding of solvent durability. The simulations showed negligible interactions between 1-IPADM-2-BOL and a model polyethylene surface, whereas strong interactions were observed on a steel interface. It was noted that the iron (Fe) atoms appeared to catalyze a reaction between two solvent molecules through mediated proton transfer, suggesting a potential mechanism of degradation (i.e., hydrolysis) that would occur for water-lean and aqueous formulations. The solvent at the interface was observed to partially degrade, leaving an organic coating on the steel interface. These simulations suggest that a steel interface could be catalytic with respect to decomposition reactions of the solvent, such as hydrolysis. They also shed light as to why organics can wet steel interfaces almost as well as plastic. This phenomenon was not observed on the polyethylene plastics, suggesting the solvent would not degrade by these means on a plastic interface, indicating that solvent lifetime would be higher on plastic packings than on stainless as hypothesized.

PNNL performed contact angle measurements to determine the wettability of water-lean solvents on different surfaces. PNNL has continued using ASTM standards (current version: ASTM D7334-08 [2013]), which requires at least six measurements at 23 ± 2°C on drops with consistent size. The contact angle measurements are especially important when determining the material composition of the reactors and their interactions with liquid reactants.

In the experimental approach, four surfaces cut in 2-inch by 2-inch pieces were used: Teflon®, Ultra High Molecular Weight Polyethylene (UHMWPE), polyetheretherketone (PEEK), and 314 stainless steel. The plastics were chosen due to their chemical and temperature resistance, while the 314 stainless steel is a material currently used in the industrial installations and serves as a benchmark. The results can be seen in Table 1.

TABLE 1: CONTACT ANGLE MEASUREMENTS OF SOLVENTS ON VARIOUS SURFACES



		Teflon®	UHMWPE	PEEK	Stainless (314)
1	1-IPADM-2-BOL/0% CO_2	avg. 72	avg. 40	avg. 30.5	avg. 42.5
2	1-IPADM-2-BOL/48% CO_2	avg. 78	avg. 55	avg. 48.5	avg. 55.5
3	2-EEMPA/0% CO_2	avg. 48	avg. 34	avg. 10	avg. 46
4	2-EEMPA/43% CO_2	avg. 69	avg. 39.5	avg. 20.5	avg. 35
5	2-EEMPA/48% CO_2, 4.3% H_2O	avg. 60	avg. 30.5	avg. 22	avg. 35.5
6	2-EEMPA/49.5% CO_2, 4.3% H_2O	avg. 62	avg. 31	avg. 20	avg. 30
7	H_2O (RO)	avg. 106	avg. 81	avg. 82	avg. 89.5
8	H_2O (tap)	avg. 115	avg. 88	avg. 95	avg. 90

*Teflon® and UHMWPE are considered hydrophobic, while 314 Stainless Steel is considered a hydrophilic surface.

The data indicates that the best wettability of the surface is achieved in the case of the PEEK surface. The results obtained for this batch of experiments indicate superiority of the plastic over the commercially used steel. This result is encouraging, as by removing steel from the system, one can slow down decomposition of the solvents and corrosion of equipment.

An experimental degradation study was performed to measure the reactions of carbamates and alkylcarbonates with O_2 and water (H_2O). Samples were subjected to stripper conditions (to mimic thermal degradation and hydrolysis) and absorber conditions (to mimic oxidation) for five weeks. The results showed that CO_2-loaded alkanolguanidine solvents are more prone to degradation reactions. Dry 1-IPADM-2-BOL showed relative stability with only approximately 10% degradation in air; however, the sample degraded 95% with water exposure. Therefore, guanidine cores are highly susceptible to hydrolysis. In contrast, the aminopyridine (2-MPMPA) and diamine (2-EEMPA) samples were found to be stable under both absorber and stripper conditions, with less than 1% decomposition observed after five weeks of testing.

Samples of 2-EEMPA and 30wt% monoethanolamine (MEA) were also tested under oxidative conditions with coated and uncoated steel interfaces. Significantly lower degradation was observed for 2-EEMPA in the presence of steel packings coated with silane compared to uncoated steel packings. This implies that passivating steel interfaces increases solvent lifetime, enabling reduced make-up rates. The coated steel packings had a less substantial effect on reducing the degradation of the aqueous amine solvent. In general, water-lean solvents are found to be more durable than aqueous solvents for thermal and oxidative degradations.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	—
Normal Boiling Point	°C	181.0	—
Normal Freezing Point	°C	<0	—
Vapor Pressure @ 15°C	bar	5E-5	—
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	—
Specific Gravity (15°C/15°C)	-	0.94	—
Specific Heat Capacity @ STP	kJ/kg-K	1.95	—
Viscosity @ 15°C	cP	11.3	—
Absorption			
Pressure	bar	1	—
Temperature	°C	40	—
Equilibrium CO_2 Loading	mol/mol	0.29	—
Heat of Absorption	kJ/mol CO_2	75	—
Solution Viscosity	cP	25	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	117	—
Equilibrium CO_2 Loading	mol/mol	0.05	—
Heat of Desorption	kJ/mol CO_2	75	—
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2.6E6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95	90
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	pending	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – Oxidative degradation and hydrolysis studies indicate solvents are more durable than 5M MEA under comparable oxidation and hydrolysis testing.

Solvent Foaming Tendency – Solvent has shown no propensity to foam under operating conditions.

Flue Gas Pretreatment Requirements – Small up-stream cooling is required to reduce water accumulation.

Solvent Makeup Requirements – Not yet available.

Waste Streams Generated – Not yet available.

Process Design Concept – Not yet available.

TABLE 3A: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEMPA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.8	—
Cost of Carbon Avoided	$/tonne CO_2	59.7	—
Capital Expenditures	$/MWhr	45.5	—
Operating Expenditures	$/MWhr	29.2	—
Cost of Electricity	$/MWhr	105.4	—

TABLE 3B: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEDIPEDA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.3	—
Cost of Carbon Avoided	$/tonne CO_2	58.7	—
Capital Expenditures	$/MWhr	45.1	—
Operating Expenditures	$/MWhr	29.1	—
Cost of Electricity	$/MWhr	104.7	—

TABLE 3C: POWER PLANT CARBON CAPTURE ECONOMICS (2-MPMPA)

Economic Values	Units	Current R&D Value	Target R&D Value

Cost of Carbon Captured	\$/tonne CO_2	40.6	—
Cost of Carbon Avoided	\$/tonne CO_2	60.6	—
Capital Expenditures	\$/MWhr	46.0	—
Operating Expenditures	\$/MWhr	29.3	—
Cost of Electricity	\$/MWhr	106.0	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Case B12B, 650-megawatt (MW) supercritical pulverized coal plant, in the National Energy Technology Laboratory's (NETL) Rev. 4 Report "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity" was used as the baseline for the techno-economic analysis (TEA). The flue gas composition, carbon capture rate, and economic assumptions were set the same as the Rev. 4 report. The coal flow rate was adjusted to achieve a net power output of 650 MW.

Scale of Validation of Technology Used in TEA – Current TEA was conducted based on the process model developed in Aspen Plus with solvent properties tested in the laboratory. All above CO_2BOL solvents have been tested in a laboratory-scale continuous flow system (LCFS) recirculating roughly 3–4 L solvent and processing simulate flue gas with 5 ppm NO, 50 ppm SO_2, and 14.4 mol% CO_2. The absorber size in the LCFS is about 2.5E^{-8} of the absorber size required in a 650-MW power plant. 2-EEMPA will be tested in a pilot-scale facility at the National Carbon Capture Center.

Qualifying Information or Assumptions – The cost of solvents (2-EEMPA, 2-EEDIPEDA, and 2-MPMPA) was assumed to be \$10/kg. To further reduce the capital and energy investment, the absorber was filled with plastic packing, while two-stage flash was used for solvent regeneration.

technology advantages

- Oxidation, foaming, aerosol formation, and corrosion issues are mitigated.
- The solvent volatility is reduced while still maintaining a favorable viscosity.
- The solvent lifetime is increased.
- Adequate wettability of solvents on plastic surfaces enables possible replacement of steel process infrastructure, reducing CAPEX and eliminating need for corrosion inhibitors.
- Passivating steel interfaces increases solvent lifetime, enabling reduced make-up rates.

R&D challenges

- There is potential for the nitration of solvents by NO_X potentially making nitrosamines.
- The chemical and physical durability of plastics in presence of solvents and the pressure, temperatures, and stresses of the system must be proven.
- Manufacturing costs for the solvents must be acceptable.

status

The project was completed in March 2021. Molecular simulations and experimental results have shown critical insights into degradation reactions of carbamates and alkylcarbonates. These results can be used for the refinement of water-lean solvents at the molecular level to increase energy barriers as a means of mitigating degradation.

available reports/technical papers/presentations

Heldebrant, D. “Molecular Refinement of Transformational Solvents for CO_2 Separations.” Presented at the 2020 CO_2 Integrated Project Review Meeting – Carbon Capture, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Heldebrant.pdf*.

Freeman, C. “Molecular Refinement of Transformational Solvents for CO_2 Separations,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/C-Freeman-PNNL-Molecular-Refinement.pdf*.

Heldebrant, D. “Accelerating the development of transformational solvent systems for CO_2 separations (FWP-65872),” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA., August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/2D-Heldebrant2-PNNL-Transformational-Solvents.pdf*.

Heldebrant, D. “Accelerating the development of transformational solvent systems for CO_2 separations: FWP-65872,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA., August 2016. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/D-Heldebrandt-PNNL-Development-of-Transformational-Solvents.pdf*.

Heldebrant, D., et.al., “Accelerating the Development of “Transformational” Solvents for CO_2 Separations.” Pacific Northwest National Laboratory. Quarterly Progress Report, Budget Period 1, May 2016. *https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-24530.pdf*.

Mixed-Salt-Based Transformational Solvent Technology for CO_2 Capture

primary project goal

The overall objective of the project is to develop a novel, water-lean, mixed-salt-based transformational solvent technology that will provide a step-change reduction in the carbon dioxide (CO_2) capture cost and energy penalties. SRI International is developing an advanced mixed-salt process (A-MSP) with the potential for accelerated scale-up to meet the U.S. Department of Energy's (DOE) Carbon Capture Program's transformational technology's goal for a coal-fired power plant. The program goals include CO_2 capture with 95% CO_2 purity and a cost of electricity at least 30% lower than a supercritical pulverized-coal (PC) power plant with CO_2 capture, or approximately $30 per tonne of CO_2 captured, ready for demonstration by 2030.

technical goals

- Demonstrate that the A-MSP can:
    - o Operate as a solvent-rich system with a very high cyclic CO_2-loading capacity (greater than 0.10 kilogram [kg] CO_2/kg of solvent).
    - o Regenerate CO_2 at greater than 10 bar at temperatures less than 120°C.
    - o Operate continuously in an integrated absorber-regenerator using simulated flue gas with 13–15% CO_2 and balance air.
- Perform thermodynamic modeling and vapor-liquid equilibrium (VLE) measurements of multi-component systems.
- Conduct kinetic measurements of CO_2 absorption of select compositions.
- Conduct solvent degradation and aerosol formation studies.
- Perform bench-scale testing of integrated absorber-regenerator system.
- Develop a rate-based model and process flowsheet and perform a techno-economic analysis (TEA) to aid identification of development pathways for technology advancement.

technical content

SRI International, in collaboration with SINTEF, Technical University of Denmark (DTU), OLI Systems Inc., and Trimeric Corporation, are utilizing the knowledge gained during a DOE-funded project (FE0012959) in the design of a mixed-salt process (MSP) that uses a solvent formulation comprised of ammonium (NH_4) and potassium (K) salt solutions to develop a transformational technology that achieves further improvements in performance. An analysis conducted by SRI indicates that inclusion of a tertiary amine to the mixed-salt formulation will yield a high CO_2-loading capacity and high-pressure solvent regeneration at low temperature, thus further reducing the energy penalty of CO_2 capture.

Bench-scale testing of SRI's first-generation MSP under FE0012959 showed that the two-component system has significant advantages over single-component systems. In the MSP chemistry, ammonia (NH_3) plays a dual role—the role of catalyst and the role of the absorbent, due to its high mobility and reactivity with CO_2. Ammonia absorbs large amounts of CO_2 at low temperature and releases

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Advanced Mixed-Salt Solvent Process

participant:

SRI International

project number:

FE0031597

predecessor projects:

N/A

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partners:

OLI Systems Inc.; SINTEF; Technical University of Denmark; Trimeric Corporation

start date:

06.01.2018

percent complete:

85%

CO_2 at high temperature and pressure, making it a highly useful chemical in CO_2 absorption formulations. By blending NH_3 with other low-capacity and low-reactivity components to suppress the undesirable high vapor pressure of NH_3, SRI has identified a next-generation A-MSP formulation that can provide a step-change reduction in CO_2 capture costs. Based on preliminary examinations, adding methyl diethanolamine (MDEA) into the MSP formulation significantly improves the capture performance, yielding a regeneration energy of 1.5–1.8 megajoules (MJ)/kg-CO_2 while operating with less than 50% water. The solvent and process parameters are provided in Table 1.

The A-MSP concept includes two isothermal absorbers, a selective regenerator, and auxiliary equipment, as shown in Figure 1. Absorber 1 operates with high-NH_3/(MDEA+K) solvent composition and absorber 2 operates with low-NH_3/(MDEA+K) solvent composition, resulting in efficient absorption and minimum NH_3 slip. In the range of 60–80% of the CO_2 in the flue gas stream is absorbed in absorber 1, and the remaining CO_2 is absorbed in absorber 2. The dual-stage absorber system reduces NH_3 carryover, resulting in less than 10 parts per million (ppm) NH_3 in the clean flue gas stream exiting the water wash. Both absorbers operate with liquid recycle using heat exchangers to remove the heat of reaction. The bottom stage operates with the highest CO_2 loading (up to 0.7 mol/mol). The CO_2-rich solutions from the absorbers are then sent to the regenerator through crossflow heat exchangers, which recover the heat from returning lean solutions. The A-MSP uses a selective regenerator to produce two CO_2-lean salt streams with high and low NH_3 content, drawn from the lower-middle and bottom stages of the regenerator. The regenerator is operated under high-pressure isobaric conditions (10–20 bar) and has a temperature gradient in the column (top ~30°C and bottom ~110°C). At high temperature, the NH_3 at the bottom of the regenerator is vaporized along with CO_2, making a lean, low-NH_3/(MDEA+K) ratio solution to be used in absorber 2. Vaporized NH_3 gets re-absorbed as the vapor moves up the regenerator column, thereby creating a high-NH_3/(MDEA+K) ratio solution in the mid-section of the regenerator for use in absorber 1. In the A-MSP design, operating the regenerator at relatively low temperature and high pressure eliminates the water stripping, thus generating an almost-dry CO_2 stream ($H_2O_{vap}/CO_2 < 0.02$) at high pressure. Figure 2 shows equilibrium modeling data comparing MSP and A-MSP systems, illustrating the high-CO_2 regeneration pressure advantage (almost doubled for 0.55 mol/mol CO_2 loading) of A-MSP with the inclusion of MDEA to the solvent. This results in a reduction of regeneration and CO_2 compression energy costs (operating cost reduction) and removal of the expensive first stage of CO_2 compression (capital cost reduction). In addition, the lower regeneration temperature and lower reboiler duty significantly reduce power plant energy loss due to steam extraction, improving the net power output of the plant (Figure 3).

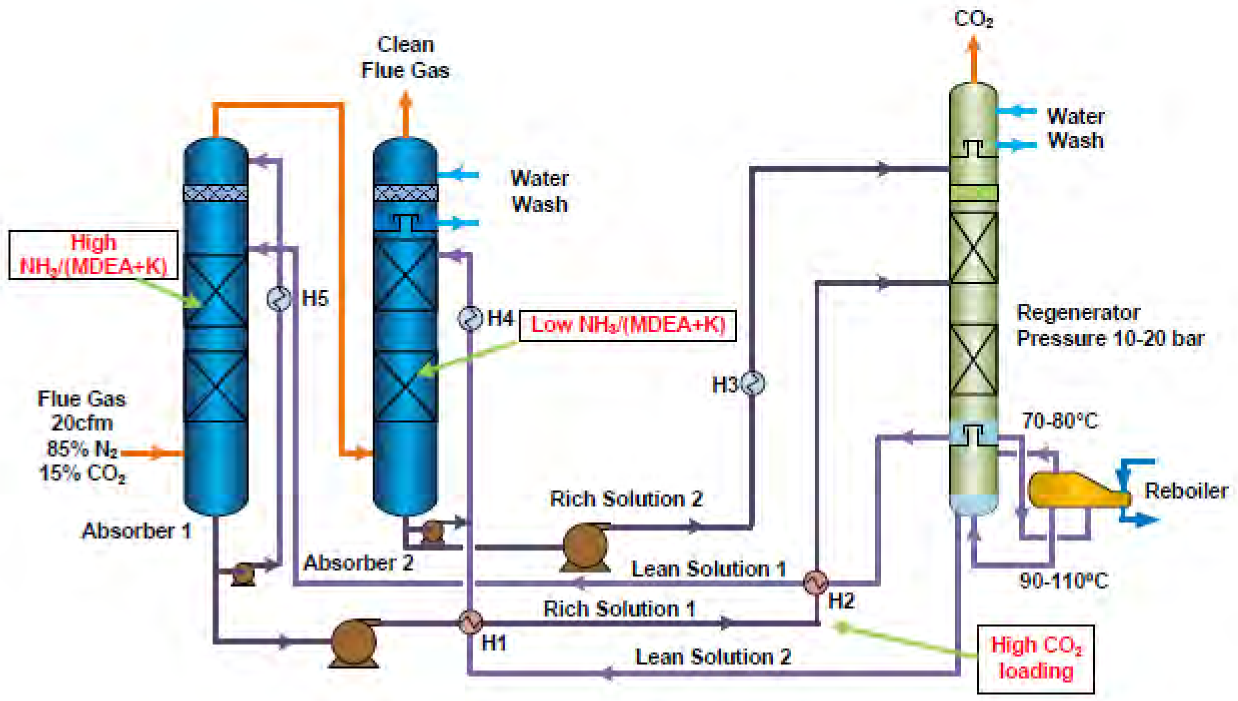


Figure 1: Conceptual process flow diagram for the A-MSP.

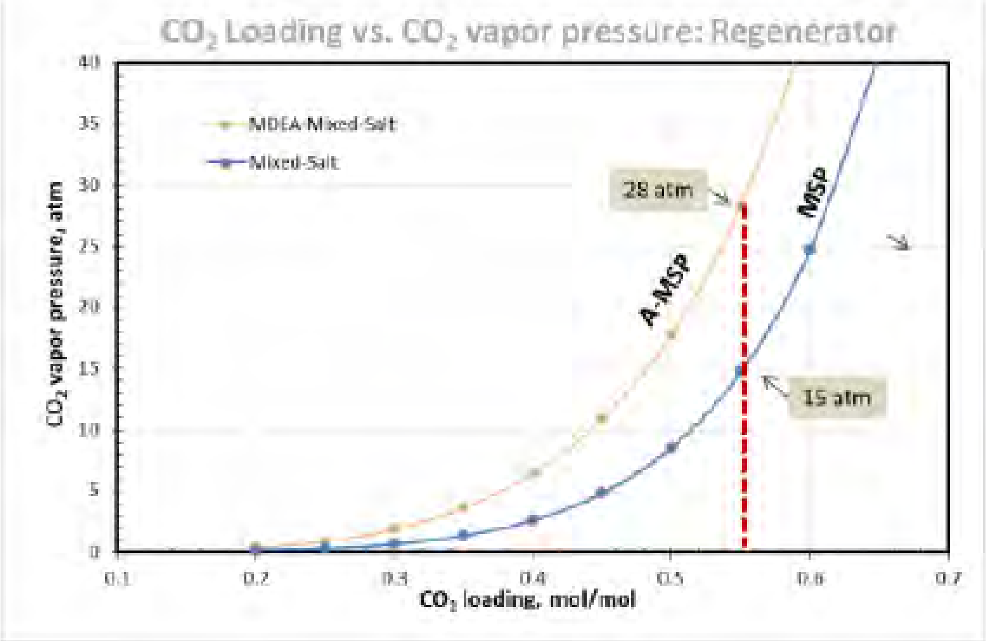


Figure 2: CO_2 loading versus CO_2 pressure at 100°C for (i) 10 molal mixed-salt and (ii) 10 molal MDEA-mixed-salt formulations.

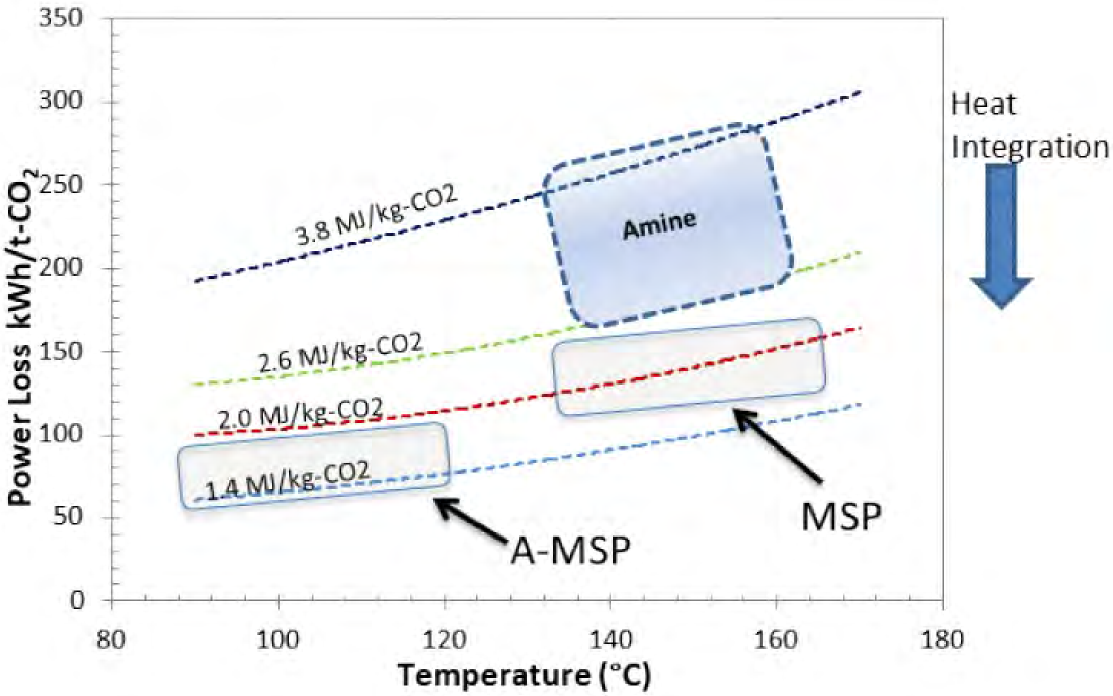
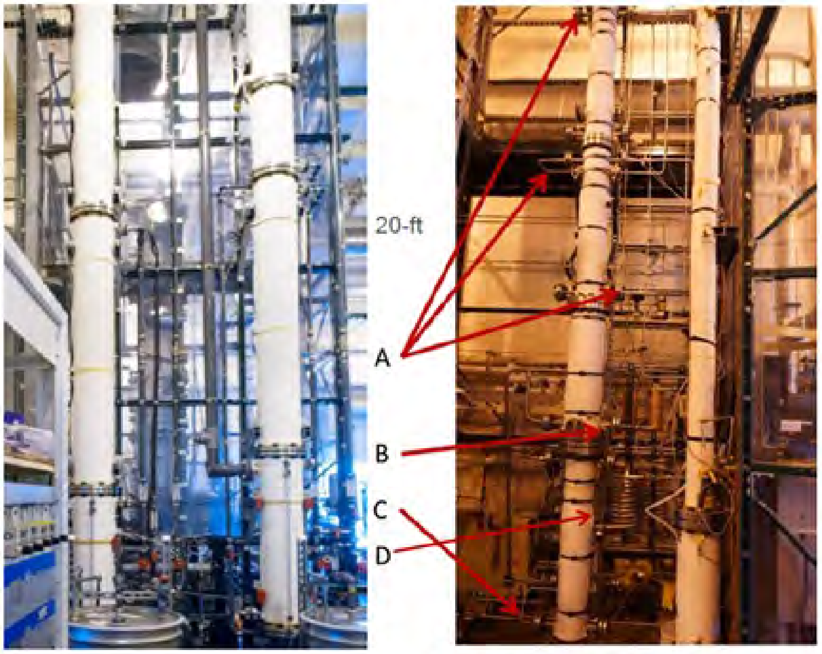


Figure 3: Power plant energy loss due to steam extraction.

Following lab-scale and small bench-scale testing, SRI's large bench-scale integrated CO_2 absorber-regenerator system (Figure 4), originally built for testing the MSP, will be used without any modifications for dynamic and steady-state testing.



A: Rich solution inlet locations
B: Discharge locations for high NH_3/K solution
C: Discharge locations for low NH_3/K solution
D: Heat exchangers (Cold rich ↔ Hot lean)

Figure 4: SRI's large bench-scale integrated absorber-regenerator system (gas flow rates up to 400 standard liters per minute).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.17	0.17
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.20-0.55	0.30-0.55
Specific Gravity (15°C/15°C)	—	1.37	1.37
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2
Viscosity @ 20°C	cP	1.6-35	1.6-35
Surface Tension @ STP	dyn/cm	73.4	73.4
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	20-40
Equilibrium CO_2 Loading	gmol CO_2/kg	1.5-3.5	2.5-3.5
Heat of Absorption	kJ/kg CO_2	795-1,136	<1,100
Solution Viscosity	cP	1.5-3.0	1.5-3.0
Desorption			
Pressure	bar	>10	10-15
Temperature	°C	120-180	140-160
Equilibrium CO_2 Loading	gmol CO_2/kg	0.2-1	0.2-0.5
Heat of Desorption	kJ/kg CO_2	1,500-2,200	<2,000

Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	—
Absorber Pressure Drop	bar		—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an monoethanolamine [MEA]-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction involves chemical absorption of CO_2 through gas/liquid phase mass transfer followed by chemical reactions in the liquid phase.

These reactions are as follows:

1. $CO_2\ (g) \leftrightarrow CO_2\ (aq)$
2. $NH_3\ (aq) + CO_2\ (aq) + H_2O\ (liq) \leftrightarrow (NH_4)HCO_3\ (aq)$
3. $(NH_4)_2CO_3 + 2CO_2\ (aq) + H_2O\ (liq) \leftrightarrow 2(NH_4)HCO_3\ (aq)$
4. $2NH_3\ (aq) + CO_2\ (aq) \leftrightarrow (NH_4)NH_2CO_2$

5. $(NH_4)NH_2CO_2$ (aq) + CO_2 (aq) + $2H_2O$ (liq) ↔ $2(NH_4)HCO_3$ (aq)
6. K_2CO_3 (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $2KHCO_3$ (aq) + catalyst
7. R1R2R3N (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $(R1R2R3NH)HCO_3$ (aq) + catalyst

where R1=R2=CH_2CH_2OH and R3=CH_3

Solvent Contaminant Resistance – High.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – The process is installed downstream of the FGD unit.

Solvent Makeup Requirements – To be determined.

Waste Streams Generated – To be determined.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	TBD	39.6
Cost of Carbon Avoided	\$/tonne CO_2	TBD	50.2
Capital Expenditures	\$/MWhr	TBD	68.8
Operating Expenditures	\$/MWhr	TBD	47.5
Cost of Electricity	\$/MWhr	TBD	116.4

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The numbers provided in the table are based on the reference plant provided by NETL for TEA analysis, found in the “Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity” report (*https://www.netl.doe.gov/energy-analysis/details?id=3745*), Revision 3.

Scale of Validation of Technology Used in TEA – Technology numbers were validated for use in the TEA analysis by modeling and laboratory testing.

Qualifying Information or Assumptions – Detailed qualifying information or assumptions regarding the economic numbers will be understood upon completion of the final TEA.

technology advantages

- Low NH_3 emissions.
- High CO_2 absorption rate and high CO_2 loading capacity.
- Reduced reboiler energy demand.
- Addition of tertiary amine to NH_4-based mixed-salt solvent reduces regeneration energy need and water use.
- Lower reboiler duty and regeneration temperature improve net power output, increasing net plant efficiency.
- Low-temperature, high-pressure regeneration of greater than 99% pure dry CO_2 reduces compression requirements.
- Oxidative degradation results show the A-MSP amine is more stable than MEA and other widely used amines.

R&D challenges

- Precipitation of solids in the absorber during cold weather conditions.
- Residual amine and/or NH_3 in exit gas stream.
- Solvent interaction with acid gases.
- Thermal management of absorber columns and regenerator.
- Volatility and corrosiveness of MDEA.

status

The project team conducted VLE measurements of various CO_2-loading levels and compositions for the regenerator side and is conducting lab-scale absorber tests to investigate reaction kinetics and CO_2 absorption capacity. SRI completed the refurbishment of the existing absorber bench-scale unit and has performed parametric testing in the unit with simulated flue gas to determine the rate of CO_2 absorption in the A-MSP solutions as a function of temperature, gas flow rate, solution composition, CO_2 loading, and liquid/gas ratio. After testing 11 different MSP solvent formulations, it was determined that a 9-molal (total) formulation comprised of potassium carbonate (K_2CO_3), NH_3, and MDEA exhibited the highest overall carbon capture efficiency. The existing MSP process model was updated to include MDEA in the solvent formulation and VLE data will be used to inform model refinements and process design. DTU has assembled a thermodynamic modeling program for the process to aid with predicting CO_2 and NH_3 isotherms under various test conditions and solvent compositions. Process kinetics assessment has been completed on the bench-scale system. Oxidative and thermal degradation studies have been completed. A preliminary A-MSP process flow sheet was developed, along with a preliminary TEA. The integrated absorption/desorption testing in SRI's large bench-scale system is currently being investigated, and a TEA will be completed in Budget Period 2.

available reports/technical papers/presentations

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_SRII.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at 2020 BP1 Review Meeting, Pittsburgh, PA, December 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10454&filename=Mixed-Salt+Based+Transformational+Solvent+Technology+for+CO2+Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Solvent.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," Project Kick-Off Meeting, September 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10459&filename=Mixed-Salt+Based+Transformational+Solvent+Technology+for+CO2+Capture.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Based-Transformational-Solvent.pdf*.

Universal Solvent Viscosity Reduction via Hydrogen Bonding Disruptors

primary project goal

Liquid Ion Solutions LLC, along with Carnegie Mellon University (CMU) and Carbon Capture Scientific LLC, is performing laboratory-scale development and evaluation of novel additives that lower the viscosity of water-lean amine solvents for post-combustion carbon dioxide (CO_2) capture. The project focuses on developing a solvent additive that minimizes the formation of long-range hydrogen bonding (HB) networks, in turn decreasing the solvent viscosity and improving the process economics.

technical goals

- Computer simulation to understand the molecular interactions in water-lean CO_2 capture solvents.
- Synthesis and characterization of HB disruptor molecules with the specific goal of significantly reducing the viscosity of water-lean carbon capture solvents in the presence of CO_2.
- Proof-of-concept performance testing to demonstrate the effectiveness of HB disruptors in lowering viscosity.
- Optimization of HB disruptor chemical structure based on insights gained from computational modeling and experimental proof-of-concept studies.
- Demonstration of the effectiveness of the optimized HB disruptors in the presence of synthetic flue gas.

technical content

Liquid Ion Solutions, in partnership with CMU and Carbon Capture Scientific, is developing additives that significantly reduce the viscosity of a water-lean amine by breaking the long-range electrostatic and HB into smaller clusters upon the absorption of CO_2, as illustrated in Figure 1. The project work includes development of computer simulation to understand the molecular interaction in water-lean CO_2 capture solvents; design, synthesis, and performance testing of HB disruptors as additives to reduce solvent viscosity; optimization of the HB disruptor; and performance testing of the optimized additive in the presence of synthetic flue gas.

The project team developed an ab initio molecular model and performed computer simulation to develop the relationship between HB and viscosity. The team then performed quantitative analysis of the additive on the viscosity of the solvent. The team completed a computational comparative study on a range of organic functional groups, such as ethers, esters, cyclic carbonates, alkanes, and ammonium salts for their effect on viscosity, gaining key insights into molecular interactions and the impact of various functional groups and molecular shapes on viscosity.

Assisted with molecular simulation insights, the project team conducted additive synthesis and testing, including a proof-of-concept study, additive screening, optimization, and synthetic flue gas testing.

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post-Combustion Power Generation PSC

key technology:

Solvents

project focus:

Novel Additives for Water-Lean Amines

participant:

Liquid Ion Solutions LLC

project number:

FE0031629

predecessor projects:

N/A

NETL project manager:

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partners:

Carbon Capture Scientific;
Carnegie Mellon University

start date:

10.01.2018

percent complete:

95%

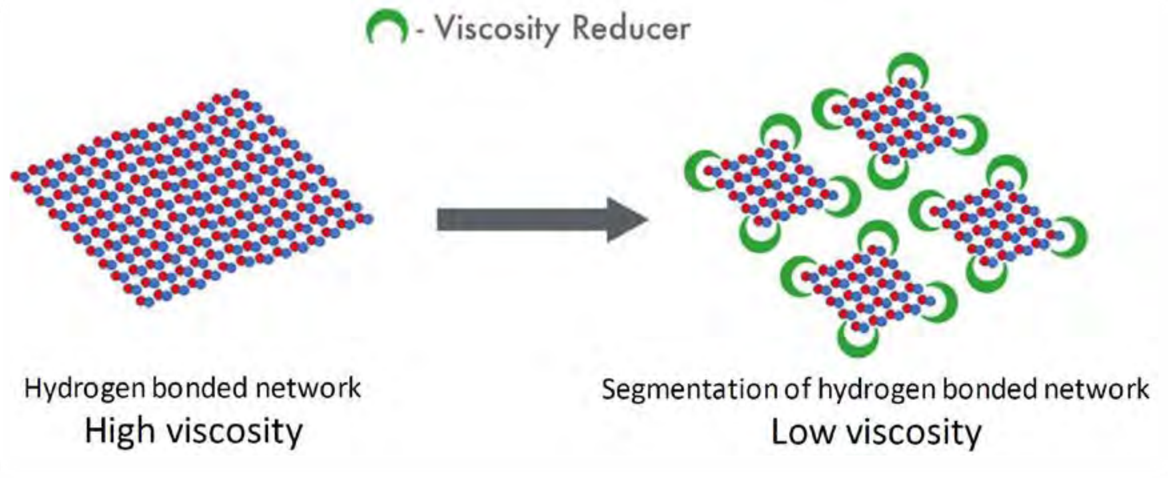

Figure 1: Illustration of fully HB network (left) and the breakage of the HB network by addition of HB acceptors (right).

The experimental proof-of-concept study proved that the HB acceptors result in significant decrease of viscosities. Detailed additive screening (exploring various functionalities and molecular structures) has been performed. Several promising additives showed excellent reduction in viscosity (30–41%) at 5% additive loading, and more than 50% viscosity reduction at 10% additive loading for the model solvents. The team also performed complex screening studies on additive loadings and mixing effect among additives using the design of experiments. Based on multiple screening experiments, one additive-solvent candidate was down-selected for synthetic flue gas testing. A 100-hour continuous absorption/desorption study was conducted under simulated flue gas using a laboratory-scale continuous capture and separation system that was constructed at Liquid Ion Solutions. No degradation (for both solvent and additive) was observed based on the gas chromatography (GC) results of the solvent samples collected from the continuous study.

Initial engineering analysis shows that a net 16% decrease in capital cost and a $3.8 per metric ton CO_2 capture cost saving is achieved by reducing the viscosity by 50%. In addition, initial health and safety assessment of the additives is also completed showing a number of these additives with low physical, chemical, and health hazards associated with them due to their chemical inertness and higher molecular weight.

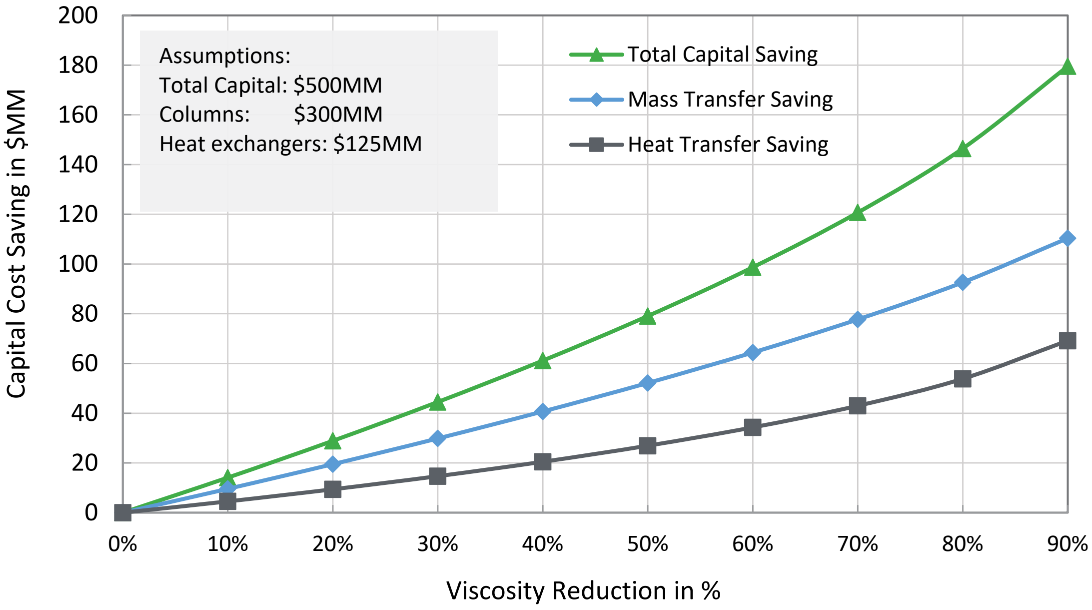

Figure 2: Impact of solvent viscosity reduction on the capital cost saving.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	140-260	<140
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15°C	Bar	<0.01	<0.01
Manufacturing Cost for Solvent	$/kg	N/A	$20 at scale
Working Solution			
Concentration	kg/kg	95/100	50/100
Specific Gravity (15°C/15°C)	—	1.02-1.07	1.05
Specific Heat Capacity @ STP	J/g/°C @25	2.0-3.0	2.0-3.0
Viscosity @ STP	cP (20 °C)	2-6	12.5
Absorption			
Pressure	Bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.48	0.48
Heat of Absorption	kJ/mol CO_2	70-80	0-80
Solution Viscosity	cP	2-6	20
Desorption			
Pressure	Bar	1	1
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.140	0.33
Heat of Desorption	kJ/mol CO_2	70-80	70-80.0
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,716,229	
CO_2 Recovery, Purity, and Pressure	% / % / bar	99/99.9/1	
Absorber Pressure Drop	Bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	200	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hour of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – Chemical (additive).

Solvent Foaming Tendency – Low.

Waste Streams Generated – CO_2.

Process Design Concept – Standard absorption/desorption column.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	54.3	56
Cost of Carbon Avoided	\$/tonne CO_2	83.3	86
Capital Expenditures	\$/MWhr	69.0	70.2
Operating Expenditures	\$/MWhr	70.3	70.6
Cost of Electricity	\$/MWhr	139.3	140.8

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The cost data in Table 2 are calculated based on the Baseline Report (2016, rev.3) Case B12B. It is assumed that the absorption/stripping columns and heat exchange equipment take 60% and 25% of the capital cost of the capture section, excluding compression and drying. It is also assumed that the viscosity of the baseline solvent (CANSOLV solvent) can be reduced 50% after adding the optimal additive developed in this project. Fifty percent is used because several additive-amine solvent systems reached viscosity lower than 50% of a PZ/MDEA (15/35 wt%) mixed aqueous solvent. It is further assumed that the unit prices of the CANSOLV solvent and the additive are \$5/kg and \$15/kg, respectively.

Scale of Validation of Technology Used in Techno-Economic Assessment (TEA) – The validity of the additive has been proven in laboratory scale and the cost reduction results are based on modeling.

Qualifying Information or Assumptions – Several new solvent candidates were also developed in this project, which could provide better economic performance than the baseline solvent. Their performance will be provided in the final technical report.

technology advantages

The development of an HB disruptor additive capable of significantly reducing the viscosity of any water-lean chemical solvent will allow for increased heat exchanger and mass transfer efficiency, thus lowering the capital and operating costs for CO_2 capture.

- Additives reduced the viscosity of amine solvents by up to 50% upon CO_2 loading.
- Amine additive solvent achieved up to 95% capture efficiency under simulated flue gas containing 15 vol% CO_2.
- Preliminary engineering analysis showed that a 50% reduction in viscosity will potentially save capital cost by about 16% and achieve $3.8/tonne CO_2 in capture cost savings without considering additive cost.
- Cost-benefit analysis demonstrated that the net benefit generated from adding a viscosity-reducing agent into the CO_2 capture solvent was significant, and that the cost of an additive itself compared to the benefit was relatively insignificant.

R&D challenges

- Determining effective additive molecules that can disrupt the overall HB network and reduce the viscosity of a water-lean solvent upon CO_2 uptake.
- Optimization of additive package maximizing viscosity-reduction effect without compromising CO_2 uptake capability for water-lean solvents.
- Identifying process conditions for the performance testing of solvent candidate using the laboratory-scale continuous capture and separation system.

status

The laboratory-scale additive development is completed. Assisted by computational simulation, the project team designed, synthesized, screened, and optimized additives to reduce viscosities of water-lean solvents. Performance testing of the optimized additive in the presence of synthetic flue gas is completed. Preliminary engineering analysis and preliminary cost-benefit analysis are completed. Currently, a refined cost-benefit analysis is underway. The project will be completed by March 31, 2022.

available reports/technical papers/presentations

Zhou, X., Brown, D., Nulwala, H., Liu, J., Li, Y., Kim, H., Chen, S., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Presented at the 2021 NETL Carbon Management and Oil Gas Research Project Review Meeting, Pittsburgh, Pa, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Zhou.pdf*.

Zhou, X., Brown, D., Nulwala, H., Liu, J., Li, Y., Kim, H., Chen, S., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/X-Zhou-LIS-Solvent-Viscosity.pdf*.

Zhou, Xu; Nulwala, Hunaid B.; Kim, Hyung; Chen, Shiaoguo, "Universal solvent viscosity reduction via hydrogen bonding disruptors," From Abstracts of Papers, 257th ACS National Meeting & Exposition, Orlando, FL, United States, March-April 2019.

Nulwala, H., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” Poster at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Nulwala-LIon-Solutions-Solvent-Viscosity-Reduction.pdf*.

Nulwala, H., “Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors,” *Project Kickoff Meeting. https://www.netl.doe.gov/projects/plp-download.aspx?id=10531&filename=Universal+Solvent+Viscosity+Reduction+via+Hydrogen+Bonding+Disruptors.pdf*.

Parametric Testing of CO_2-Binding Organic Liquids (CO_2BOLs)

primary project goal

Pacific Northwest National Laboratory (PNNL) is performing testing and optimization of three advanced carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) water-lean formulations for post-combustion CO_2 capture. PNNL leverages its carbon capture laboratory infrastructure and testing methodologies to collect comprehensive physical and thermodynamic property test data for each solvent. Aspen Plus® models utilize the physical property translations of the collected data to project the energetics (e.g., reboiler duty, parasitic load) and preliminary capture costs.

technical goals

- Accelerate scale-up focus for three third-generation, low-viscosity CO_2BOL solvent formulations (two from aminopyridine [AP] class and one from diamine [DA] class).
- Perform testing and evaluation at laboratory scale to inform a techno-economic assessment (TEA) of the solvents' performance toward the U.S. Department of Energy's (DOE) $40/tonne CO_2 target.
- Engage new industry partners for subsequent scale-up and testing at the National Carbon Capture Center (NCCC) or an equivalent facility.

technical content

Under prior DOE-funded studies, PNNL developed a number of single-component, water-lean CO_2BOLs as post-combustion CO_2 capture solvents. One DA formulation in particular, N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), was evaluated extensively, achieving 40 hours of steady-state CO_2 capture rates of at least 90% on simulated flue gas. While 2-EEMPA shows promise as a single-component water-lean solvent and is being scaled up with industrial partners, it is unclear if EEMPA has the highest chemical durability, lowest reboiler duty, or lowest total costs of capture that water-lean solvents can achieve. This offers an opportunity to identify and develop other unique CO_2BOLs solvents with their own intellectual property portfolios that could be licensed independently and, therefore, draw in other industrial partners.

In DOE-funded project FWP-72396, PNNL completed a study of AP and DA solvent classes to identify solvents with the lowest volatility and viscosity, respectively. The result of that work led to the design, synthesis, and testing of two viable derivatives from each of the DA and AP solvent classes. The four solvents were synthesized and tested for vapor-liquid equilibrium (VLE), viscosity, and mass transfer measurements in PNNL's custom pressure-volume-temperature (PVT) cell, and were found to have comparable CO_2 bonding strength to that of the leading 2-EEMPA solvent, making them suitable for post-combustion CO_2 capture. Three final candidate CO_2BOL solvents were shown to exhibit CO_2-rich viscosities as low as 2.9 centipoise (cP) and to have the potential to meet or exceed PNNL's EEMPA solvent in performance: N^1-(2-ethoxyethyl)-N^2,N^2-diisopropylethane-1,2-diamine

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
CO_2-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-76270

predecessor project:
FWP-72396

NETL project manager:
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principal investigator:
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partners:
Carbon Capture Simulation for Industry Impact

start date:
05.01.2020

percent complete:
80%

(EEDIDA), (2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine (MPMEA), and (3-methoxy-N-(pyridin-2-ylmethyl)propan-1-amine (MPMPA). This project is designed to measure the critical data needed to project performance of these CO_2BOL water-lean formulations for post-combustion CO_2 capture, ultimately enabling slip stream testing and subsequent industry adoption.

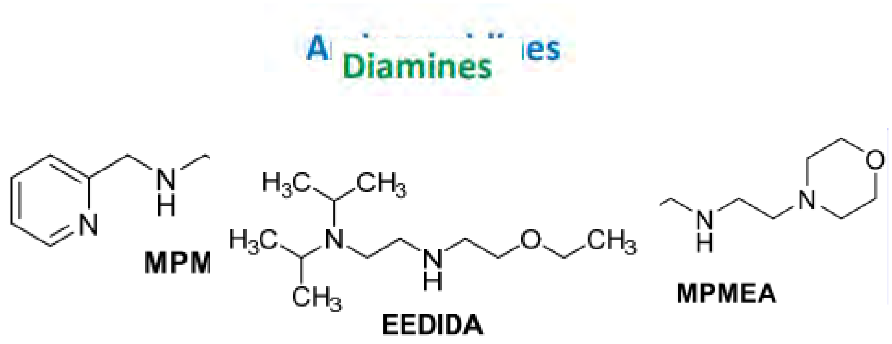

Figure 1: Final CO_2BOL derivatives for evaluation.

The aim of this project is to verify that MPMPA, MPMEA, and EEDIDA are energetically efficient and cost-effective post-combustion CO_2 capture solvents. The chemical durability of the solvents is expected to be at least comparable to that of monoethanolamine (MEA) with similar, if not reduced, solvent makeup rate. The project goal is to show that all solvents exhibit steady-state capture of 90% CO_2 on simulated flue gas for a period of at least 40 hours with and without 5 wt% water at acceptable liquid/gas (L/G) ratios (~4). The reboiler duty is projected to be 2 GJ/tonne CO_2 or less in at least one process configuration (e.g., inter-heated column or lean vapor compressor), with each solvent having at least one configuration with total costs of capture at or below $50/tonne CO_2. EEDIDA is expected to behave comparably to 2-EEMPA, albeit with lower energies associated with pumping and heat exchange performance due to its lower viscosity. The aromatic AP solvents are expected to be lower in enthalpy as they are more hydrophobic, which could lower the steady-state water loadings and lessen any upstream flue gas refrigeration needs to manage water, though this may be offset by the chilling required to prevent solvent loss from the top of the absorber due to higher vapor pressures than 2-EEMPA. Nevertheless, the preliminary total costs of capture for the AP solvents are still expected to net out at favorable overall energy and cost performance.

Each of the solvents are being scaled up for comprehensive property testing on PNNL's custom PVT, wetted-wall contactor, and laboratory continuous flow system (LCFS) test apparatuses. A myriad of tests are used to measure physical and thermodynamic properties, which are then used to construct thermodynamic models in Aspen Plus. Key measurements include VLE, viscosity, density, thermal conductivity, vapor pressure, flashpoint, contact angles, and liquid-film mass transfer coefficients; preliminary chemical durability studies of flue gas impurities (i.e., sulfur oxide [SO_X], nitrogen oxide [NO_X], and oxygen [O_2]); and foaming and aerosol formation studies. PNNL's LCFS is used to perform a set of parametric tests to collect solvent performance data at various absorber temperatures, gas and liquid flow rates, and solvent lean loading. Initial testing on the LCFS is being performed to establish the steady-state water loading—estimated to be 5 wt%, but requires continuous operation to verify. The next stage of testing is on simulated flue gas for 40 or more hours, targeting steady-state removal of 90% of the CO_2, resulting in data generated that can be used to project solvent lifetime and subsequent makeup rates. Routine sampling is being performed to quantify heat-stable salt formation with SO_X, NO_X, potential hydrolysis, and oxidative degradation of DA formulations. A TEA is being performed such that PNNL can engage potential commercialization partners.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value		Target R&D Value
		EEDIDA	MPMPA	
Molecular Weight	mol^{-1}	206	180	—
Normal Boiling Point	°C	158	157	—

Normal Freezing Point	°C	<0	<0	—
Vapor Pressure @ 15°C	bar	2×10^{-4}	3×10^{-5}	—
Manufacturing Cost for Solvent	\$/kg	10	10	5
Working Solution				
Concentration	kg/kg	0.96	0.97	—
Specific Gravity (15°C/15°C)	-	0.86	0.93	—
Specific Heat Capacity @ STP	kJ/kg-K	2.02	2.36	—
Viscosity @ 15°C	cP	4.72	12.03	—
Absorption				
Pressure	bar	1.01	1.01	—
Temperature	°C	35	35	—
Equilibrium CO_2 Loading	mol/mol	0.35	0.27	—
Heat of Absorption	kJ/mol CO_2	76	64	—
Solution Viscosity	cP	18.4	29.2	—
Pressure	bar	2.3	1.8	—
Temperature	°C	87	101	—
Equilibrium CO_2 Loading	mol/mol	0.11	0.07	—
Heat of Desorption	kJ/mol CO_2	76	64	—
Proposed Module Design		*(for equipment developers)*		
Flue Gas Flowrate	kg/hr	3.35E6		
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	150
Absorber Pressure Drop	bar	<0.1		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	pending		

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Foaming Tendency – Depending on the tendency to foam, anti-foaming agents may need to be added to the solvents during testing.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO_2) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively. Fuel gas chilling is required to maintain water balance in the system.

Process Design Concept – Two-stage flash configuration is considered for solvent regeneration for less capital investment and less energy consumption for CO_2 compression.

TABLE 2A: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEDIDA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	39.2	—
Cost of Carbon Avoided	\$/tonne CO_2	58.7	—
Capital Expenditures	\$/MWhr	45.1	—
Operating Expenditures	\$/MWhr	59.6	—
Cost of Electricity	\$/MWhr	104.7	—

TABLE 2B: POWER PLANT CARBON CAPTURE ECONOMICS (2-MPMPA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	40.6	—
Cost of Carbon Avoided	\$/tonne CO_2	60.6	—
Capital Expenditures	\$/MWhr	46.0	—
Operating Expenditures	\$/MWhr	60.0	—
Cost of Electricity	\$/MWhr	106.0	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced, including fuel cost and variable and fixed operating costs.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced, including fuel cost, variable and fixed operating costs, and transportation, sequestration, and monitoring cost.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Other Parameter Descriptions:

Calculations Basis – Case B12B, a 650-megawatt (MW) supercritical pulverized coal plant, in NETL's Rev. 4 Report, "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity," was used as the baseline for TEA. The flue gas composition, carbon capture rate, and economic assumptions were set the same as the Rev 4 report. The coal flow rate was adjusted to achieve a net power output of 650 MW.

Scale of Validation of Technology Used in TEA – Current TEA was conducted based on the process model developed in Aspen Plus. These CO_2BOLs have been tested in an LCFS recirculating roughly 3–4 L solvent and processing simulate flue gas. The absorber size in the LCFS is about 2.5E-8 of the absorber size required in a 650-MW power plant.

Qualifying Information or Assumptions – The manufacturing cost of solvent is set to $10/kg.

technology advantages

- Low solvent volatility.
- Lower CO_2-rich viscosity than early versions of CO_2BOL solvents.
- Significantly lower regeneration energy compared to aqueous amines.
- The project leverages active collaborations with industry, national labs, and academia through the Carbon Capture Simulation for Industry Impact (CCSI^2) Program.

R&D challenges

- The hydrophobic MPMPA and MPMEA solvents may promote foaming during continuous flow testing on PNNL's LCFS testing cart, which could lead to decreased capture efficiency, disrupt pumping flow rates, and potentially aerosolize solvent outside of the absorber column.
- The higher viscosity may adversely impact the performance of the AP solvents during testing and prohibit collection of data in an operable L/G regime.
- Chemical impurities (NO_X and SO_X) in flue gas during continuous-flow testing may adversely impact solvent performance by forming heat-stable salts or nitrosamines.
- Achieving DOE's $40/tonne cost target.

status

The project team has synthesized more than five liters of EEDIDA and three-liter quantity of MPMPA solvents and completed solvent kinetics and VLE measurements on the solvents. The solvent 2-EEDIDA was shown to have lower viscosity and higher selectivity than 2-EEMPA and has achieved 40 hours of steady-state CO_2 capture of 90% with no foaming or aerosols during continuous flow testing on simulated flue gas. In general, MPMPA has similar VLE and kinetics as EEMPA and EEDIDA solvents. The strength of MPMPA as a CO_2 solvent is between EEMPA and EEDIDA. At a similar set of lean- and rich-operating conditions, MPMPA solvent's viscosity is less than that of EEMPA and greater than EEDIDA, while the kinetics of MPMPA are similar to EEMPA. A preliminary TEA suggests that EEDIDA will have a CO_2 capture cost that is $1.40/tonne less than that of EEEMPA.

MPMEA was produced in three-liter quantity at approximately 90% purity, which is a lower purity grade than the previous two solvent candidates; the initial VLE and kinetics measurements of MPMEA were completed and heat of solution was estimated. The data, compared with known data on EEMPA, indicate that MPMEA is slightly weaker with slower kinetics and somewhat higher viscosity. Additional PVT cell measurements on MPMEA with various amounts of water are being performed, followed by continuous flow testing on simulated flue gas.

available reports/technical papers/presentations

Heldebrant, D. “Parametric Testing of CO_2BOLs to Enable Industry Adoption (FWP-76270).” NETL Carbon Management and Oil and Gas Research Project Review Meeting - Point Source Capture - Lab, Bench, and Pilot-Scale Research, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Heldebrant.pdf*.

Heldebrant, D. “Molecular Refinement of Transformational Solvents for CO_2 Separations,” Presented at the 2020 CO_2 Integrated Project Review Meeting – Carbon Capture, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Heldebrant.pdf*.

Freeman, C. “Molecular Refinement of Transformational Solvents for CO_2 Separations,” Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/C-Freeman-PNNL-Molecular-Refinement.pdf*.

“Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration,” Presented at the 2018 NETL CO_2 Capture Technology Meeting, August 13, 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.

Reducing the Degradation of Carbon Capture Solvents

primary project goal

Pacific Northwest National Laboratory (PNNL) is conducting research to mitigate common mechanisms of solvent degradation and byproduct formation in carbon dioxide (CO_2) capture processes. Research and development (R&D) efforts focus on studying the effects of steel interfaces on oxidation and nitrosation for both aqueous and water-lean solvents and studying the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation) and design new formulations that are resistant to these chemical degradations.

technical goals

- Develop fundamental understanding of degradation mechanisms for multiple solvent components on steel interfaces such that oxidative degradations from oxygen (O_2) and nitrogen oxide (NO_X) can be mitigated.
- Study the effects of steel interfaces on oxidation and nitrosation for up to six solvents from aqueous and water-lean classes (three from each).
- Develop experimental and computational studies of solvent degradation for neat solvents and then solvents in the presence of 304 carbon and 316 stainless steels uncoated or treated with urethane or imidazole coatings.
- Downselect solvents/conditions for confirmation testing in PNNL's small-scale continuous testing platform.
- Evaluate two CO_2BOLs, including N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), as an additive in commercial aqueous solvents with the aim of fast-tracking commercialization for aqueous solvents.
- Perform an initial techno-economic analysis (TEA) based on the material property measurements.
- Develop molecular model and batch testing to ascertain degradation/byproduct behavior for the most viable aqueous blends identified in the earlier tasks.

technical content

Commercial and pre-commercial solvents for CO_2 capture from flue gas sources have advanced considerably over the years. R&D has focused on lowering overall regeneration energy via solvent chemistry advances and related process development. Additionally, work on quantifying and reducing solvent degradation was undertaken in the previous DOE-funded Field Work Proposal (FWP)-72396. Solvent degradation not only impacts solvent costs, but can ultimately hinder fielding if hazardous products are formed (e.g., carcinogenic nitrosamines). The purpose of this research is to leverage prior PNNL investigations on the fundamental understanding of degradation mechanisms of multiple solvent components. PNNL's molecular modeling experts provide mechanistic insights to observed degradation pathways and potential chemistry for additives or process modifications for ultimate mitigation. Other degradation measurements for solvents, such as data from SINTEF's solvent degradation test rig, are also used for validation. Further, there is interest in understanding the impacts of intentional dilution of PNNL's water-lean CO_2BOLs in aqueous solvent blends as a means of commercially fast-tracking those solvents. This fast-track approach requires an understanding of solvent performance impacts, as well as any unique degradation/byproduct impacts.

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post Combustion Power Generation PSC

key technology:

Solvents

project focus:

Methods for Mitigating Mechanisms of Solvent Degradation

participant:

Pacific Northwest National Laboratory (PNNL)

project number:

FWP-77217

predecessor projects:

FWP-72396

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Carl Laird
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partners:

N/A

start date:

01.01.2021

percent complete:

54%

PNNL's previous work in FWP-72396 showed a previously undiscovered solvent degradation that occurs on the interfaces of stainless steels. In this study, PNNL had discovered direct chelation of specific chemical motifs of carbon capture solvents directly coordinating to stainless steel interfaces and chemically activating them for degradations such as hydrolysis and oxidation (Figure 1). It is believed that the chromium oxide (CrO) coating that makes stainless steel corrosion resistant acts as the catalyst for oxidative degradation reactions with O_2 and NO_X. Chromium oxides are known oxidative catalysts for alcohols and amines, and unsurprisingly, previous studies indicated that the structural motifs that showed the highest deactivation in the presence of steels were those that contained alcohols and imines, with the former present in all alkanolamines and the latter in the CO_2BOL alkanol guanidine solvent class. The finding that steel interfaces directly coordinate and activate specific chemical moieties means that all carbon capture solvents are susceptible to these degradations. Learning how to stop these catalytic activations for decomposition reactions provides a new means to increase solvent lifetime for all solvent-based processes. Thus, this research effort aims to shut down this newly discovered mechanism of catalytic decomposition by steel interfaces for both aqueous and water-lean solvents by simply passivating the interface with durable organic coatings. Further, if the CrO coating on stainless is the culprit, passivation of a less expensive carbon steel (304) with a chemically durable organic coating could result in significant cost-savings for infrastructure and avoid the use of costly 316 stainless steel.

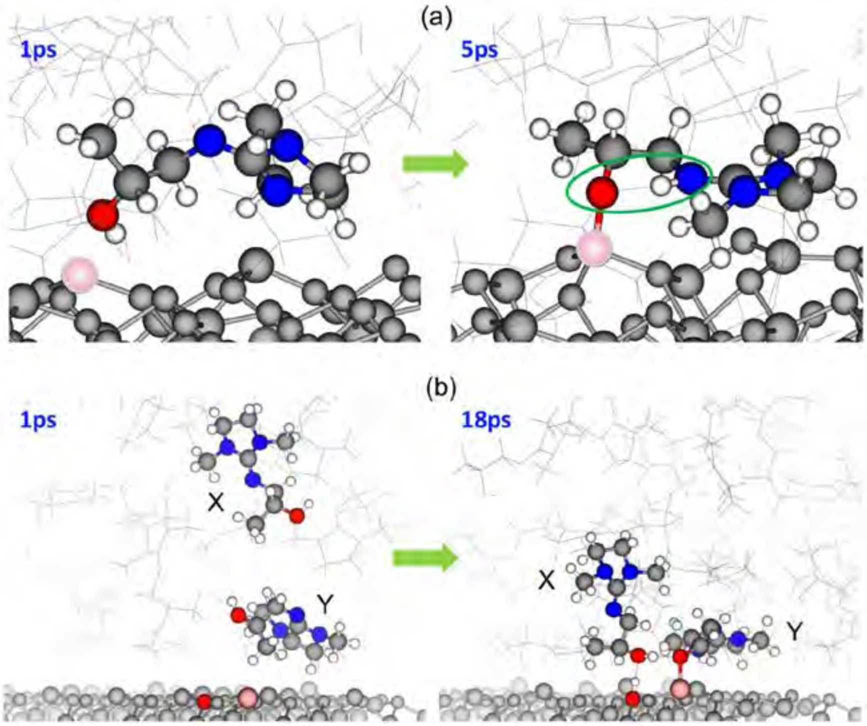

Figure 1: Representative interfacial activation of a water-lean solvent by stainless steel. 1-IPADM-2-BOL/hematite(steel) interface: (a) structure of a molecule right at the solid surface at 1 picosecond (ps) and 5 ps of an Ab initio molecular dynamics (AIMD) simulation, the surface atom in pink indicates the iron atom that assists the proton transfer from the OH group to an N atom of the same molecule; (b) structure of two molecules X and Y at 1 ps and 18 ps of the same AIMD simulation, surface atoms O (red) and Fe (pink) directly assisted the proton transfer from X to the surface and from Y to X. Most of surface atoms and surround molecules are in grey for clarification.

The project team showed that they could increase solvent lifetime by as much as 50% by simply removing contact with a steel interface. The retardation of chemical degradation of solvents was achieved by removing the steel interfaces that were acting as catalysts for the degradation reactions. Thus, removal or passivation of the interface had the effect of increasing the degradation activation energies (thermal, oxidation, hydrolysis) for three solvents by approximately 2,000–3,000 calorie (cal)/mol. PNNL aims to show that comparable retardation could be achieved for other modes of amine degradation in solvent-based post-combustion CO_2 capture processes.

Reactions of carbon capture solvents with NO_X remains a challenge for solvent developers as nitrosation results in the formation of potentially carcinogenic nitrosamines. Often, nitrosation cannot be avoided, and multiple solvent formulations have had to be used with caution (e.g., piperazine, 2-AMP) or outright abandoned (e.g., a subcomponent in an experimental Fluor solvent) due to unacceptable levels of nitrosamine formation. Nitrosation occurs via an oxidation reaction, which PNNL hypothesizes to be catalyzed by stainless steel interfaces, not just dissolved metals that accumulate in the solvents from corrosion. Nitrosamines are specifically problematic for secondary amine chemical moieties, which are often utilized due to their more favorable energetics as compared to primary amines such as monoethanolamine (MEA). Thus, if nitrosation could be mitigated by coating steel interfaces, previously established energetically favorable and cost-effective solvents could be revitalized and rapidly expedited for commercialization.

Mechanistic studies are being performed systematically with dissolved metal catalysts to determine which, if any, catalyze the nitrosation reaction. With this data, PNNL is designing new aqueous amine formulations that have different functional groups that would disfavor nitrosation. PNNL is also performing experimental and computational studies of solvent degradation for neat solvents and solvents in the presence of 304 carbon and 316 stainless steels that are both uncoated and treated with urethane or imidazole coatings. The goal is to confirm that coated 304 steels do not catalyze oxidative degradations and are resistant to corrosion.

There is interest in using PNNL's water-lean CO_2BOLs solvents to initially enable more conservative concentrations in aqueous blends, despite the outstanding performance with minimal water. The logic in this interest is that one commercialization barrier is the risk to technology providers of using a new solvent in water-lean form in existing/initial commercial equipment. Fluor used this approach when developing their latest Econamine FG+ solvent, which increased the solvent concentration from approximately 30% up to 50%. PNNL is assessing two CO_2BOLs as active additives to commercial aqueous solvents with water loading ranging from 50–80%. The project team is utilizing molecular modeling and batch testing to ascertain degradation/byproduct behavior. The most viable aqueous blends are then being subjected to steady-state continuous testing using simulated coal-derived flue gas. By using a CO_2BOL solvent as an active ingredient in an aqueous system, higher initial concentrations would be achievable, along with the prospect to drive those loadings up to greater than 90% over time, reducing the overall commercialization risk.

There are four primary goals of this project:

- Mitigate the mechanism of catalytic oxidative decomposition by steel interfaces for both aqueous and water-lean solvents that have been assessed in various platforms, including the SINTEF degradation test rig, by simply passivating the interface with novel monolayer coatings.
- Enable utilization of cheaper carbon steel (304) by modifying the surface with chemically novel monolayer organic coatings, resulting in significant cost-savings for infrastructure by avoiding the use of costly 316 stainless steel.
- Evaluate water-lean CO_2BOLs as active ingredients in next-generation aqueous solvent systems, utilizing higher initial concentrations with the goal to increase loadings up to greater than 90% over time, thus reducing the overall commercialization risk of water-lean solvents.
- Perform steady-state continuous flow testing using PNNL's laboratory-continuous flow system (LCFS) for the best-performing aqueous and water lean solvents to demonstrate, for at least for 72 hours, achieving 90% capture from simulated coal-derived flue gas (15% CO_2, 84% N_2 with sulfur oxide [SO_X], NO_X, O_2) and validate TEA projections.

technology advantages

- Potential to shut down oxidative decomposition by steel interfaces through passivation of the liquid-solid interface.
- Enable utilization of less-expensive carbon steel (304).

R&D challenges

- Demonstrate a minimum of 72 hours of continuous flow testing achieving greater than 95% capture from simulated coal-derived flue gas.

status

PNNL is currently working on identifying candidate steel coatings and batch testing multi-solvents and additives, along with coated and uncoated steels. Additionally, molecular modeling is being developed concurrently to theoretically study the solvent properties; these are being correlated to the experimental test data being collected from the small-scale continuous testing apparatus.

available reports/technical papers/presentations

Koech, P., "Reducing the Degradation of Carbon Capture Solvents," Project kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11576&filename=Reducing+Degradation+of+Carbon+Capture+Solvents.pptx*.

Koech, P., "Reducing the Degradation of Carbon Capture Solvents," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Koech.pdf*.

Process Intensification for Carbon Capture

primary project goal

Altex Technologies Corporation, in partnership with Pennsylvania State University (PSU), previously developed the integrated temperature and pressure swing (ITAPS) carbon capture system. The ITAPS system utilizes advanced molecular basket sorbents (MBSs) on microchannel heat exchangers, which can be quickly cycled between carbon dioxide (CO_2) sorption from coal-derived syngas and desorption into low-pressure steam exhausted from steam turbines in an integrated gasification combined cycle (IGCC) power system. This would replace the typical three-stage Selexol system (for acid gas removal and pre-combustion carbon capture in the context of IGCC) with smaller and more energy-efficient desorption and sorption units.

The project is currently in Phase IIB, with the goal of developing the Compact Rapid Cycling CO_2 Capture (CRC3) system that would extend the concept of using the MBSs on microchannel heat exchangers to post-combustion applications. Also, work is continuing to reduce the size (and therefore costs) of the Altex CO_2 capture system by coating both sides of the heat exchanger with a sorbent with rapid sorption-desorption kinetics. Current objectives are to design a prototype-scale system for CRC3 to improve the MBSs for higher heat- and mass-transfer rates, to fabricate and test a prototype-scale CRC3 sorbing unit on actual flue gas, and to perform techno-economic analysis (TEA) of the CRC3 system integrated into a large-scale power plant.

technical goals

- Improve sorbent capacity and sorption/desorption rates.
- Demonstrate heat integration of sorption and desorption processes.
- Conduct prototype-scale testing of a post-combustion capture-geared prototype unit on actual flue gas at 10–50 standard liters per minute (slpm), equivalent to 0.2–1.0 kilowatt-electric (kWe).

technical content

The Altex team previously developed the ITAPS process with a view to produce a low-cost CO_2 capture technology that leverages process intensification principles (i.e., process capital and energy costs of the capture systems are shared with other unit operations of the power plant). In ITAPS, Altex-developed microchannel heat exchangers were wash-coated with PSU's advanced MBSs. By wash-coating the MBS on the microchannel heat exchanger, high heat- and mass-transfer rates were obtained. These high rates allow for quick cycling between CO_2 sorption and desorption. This should allow smaller sorption units with a lower capital cost than a typical three-stage Selexol system. Operating costs are also lower than a three-stage Selexol system because the system can operate at lower pressures and does not require circulation of a liquid amine sorbent. The system can also be integrated with the power plant steam loop to improve energy efficiency; the heat of sorption can be used to preheat the boiler feedwater, while the heat of desorption can be used to condense about 50% of the steam turbine exhaust. In terms of process integration, Figure 1 depicts the ITAPS units' process with boiler feed water flows and steam turbine flows (for sorption and desorption modes,

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Molecular Basket Sorbents on Microchannel Heat Exchangers

participant:
Altex Technologies Corporation

project number:
SC0013823

predecessor projects:
N/A

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partners:
Pennsylvania State University; NCCC

start date:
06.08.2015

percent complete:
93% (combined Phases I, II, & IIB)

respectively), which would be encountered in integrating an ITAPS system within the context of an IGCC cycle or a traditional power plant.

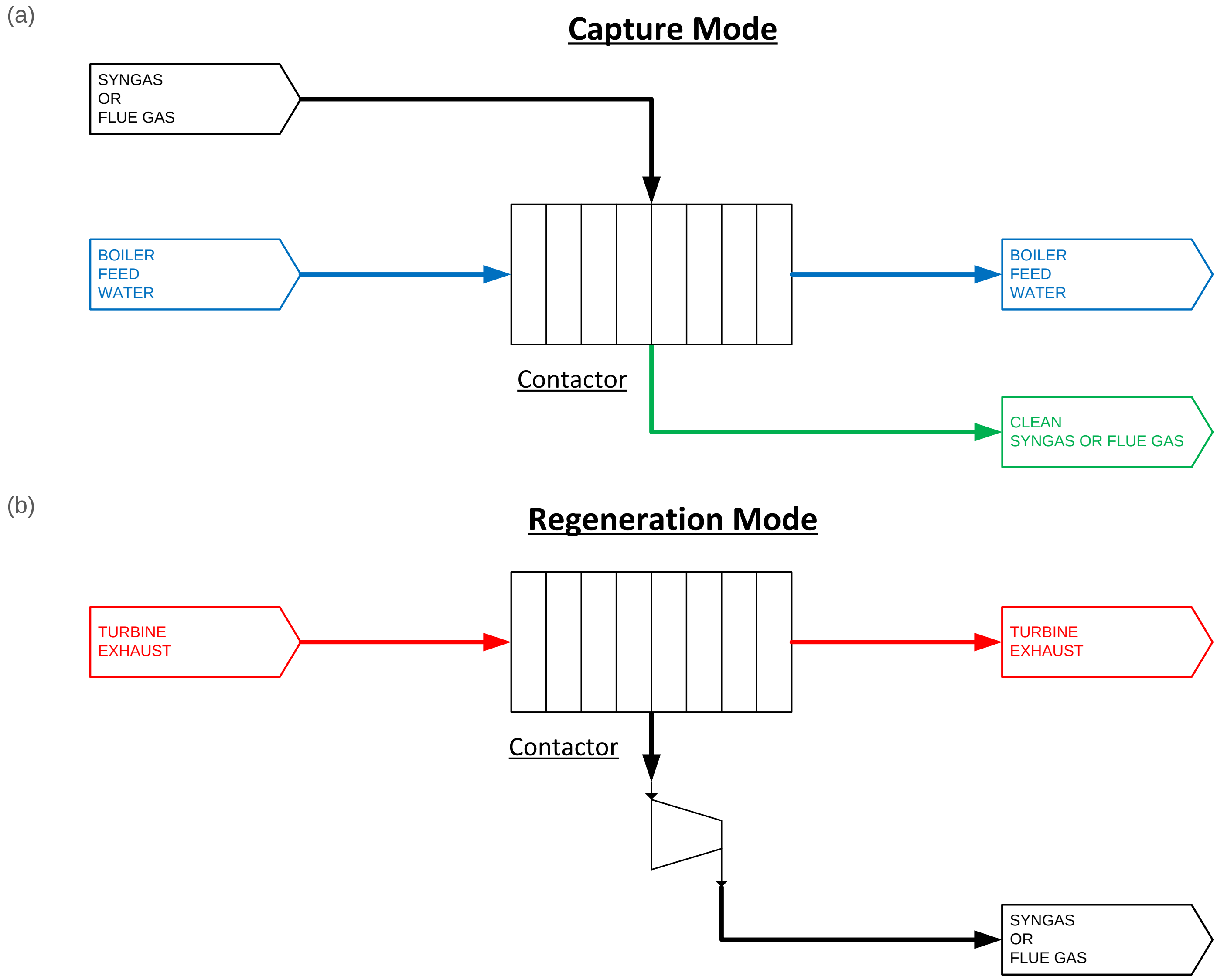

Figure 1: Simplified process flow diagram for the Altex integrated temperature and pressure swing carbon capture process. (a) Capture Mode—Cooling provided by boiler feed water; (b) Regeneration Mode—Heating provided by turbine exhaust.

PSU has been responsible for development of the sorbents they term as MBSs. The idea is to load CO_2-philic polymers such as polyethyleneimine (PEI) onto high-surface-area nano-porous inorganic materials such as MCM-41 and SBA-15, thereby increasing the accessible sorption sites per weight/volume of sorbent and improving the mass-transfer rate in sorption/desorption processes by increasing the gas-PEI interface. These sorbents can selectively adsorb large quantities of CO_2 compared to typical sorbents such as zeolites or activated carbons. The sorbents also pack CO_2 in a condensed form in the mesoporous molecular sieve basket and hence show a high CO_2 capacity and selectivity. The basic idea for preparation of MBS is illustrated in Figure 2.

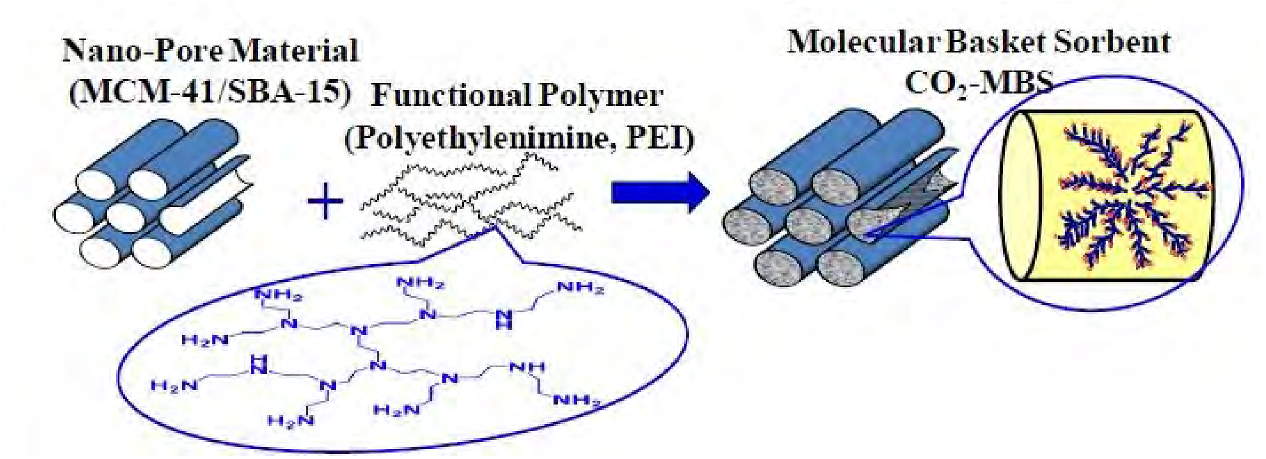

Figure 2: Principle for preparation of MBS.

The sorbents are applied by wash-coating the surfaces of microchannel heat exchangers. Altex is leveraging their expertise in design of these heat exchangers, which have been deployed in a wide range of sizes (fractions of kW to multiple megawatt [MW] capacities); materials (aluminum, copper, stainless steel, high-temperature alloys, corrosion-resistant alloys); counter-flow and cross-flow configurations; for various types of fluid flows; and in many fields, including oil and gas platform processes, separators, liquefied natural gas (LNG) processing, chillers, heat pumps, fuels reforming, waste heat power systems, and electronics cooling applications. For ITAPS, Altex developed the bench-scale prototype depicted in Figure 3. Note that finned inserts within the unit provide ample surface area onto which MBS can be wash-coated. In the pre-combustion capture case, the process stream of syngas containing CO_2 passes through the channels, and on the utility side, cooling water provides withdrawal of heat; in regeneration, steam would be passed through the channels to purge out the captured CO_2. Extensive surface area facilitates efficient heat transfer needed to accomplish the sorption and desorption steps for capture of CO_2.

Figure 3: Illustration of ITAPS microchannel heat exchanger units/reactors. Highly efficient, low-cost heat exchanger.

In earlier project phases, PSU advanced the MBS material to improve the CO_2 capacity, and Altex demonstrated and established the feasibility of wash-coating this sorbent onto the microchannel heat exchanger. Advancements were made in both improving the mechanism of loading of the polymer into the solid matrix of the sorbent (low-cost fumed silica has been used in place of high-cost mesoporous silica, and sorbent performance improved by incorporating 3-aminopropyl triethoxysilane [APTES] along with PEI in the polymer formulation) and in improving the process for wash-coating the reactor (a single-step wash-coating method incorporating fumed silica, APTES, and PEI was devised, eliminating a separate impregnation step).

The bench-scale system prototype was tested for multiple cycles of CO_2 sorption/desorption, validating the feasibility of cycling and heat recovery. Data from these tests were used to determine the required wash-coat thickness needed to meet the target cost of electricity (COE) and ensure that this thickness can maintain a high effectiveness. From findings of the testing, analysis showed that the ITAPS process could significantly reduce cost of capture and COE.

Currently, the project is extending application of this technology into the area of post-combustion CO_2 capture. Figure 4 depicts the process concept for the CRC3 system, which deploys the Altex technology to capture of CO_2 from post-combustion flue gas.

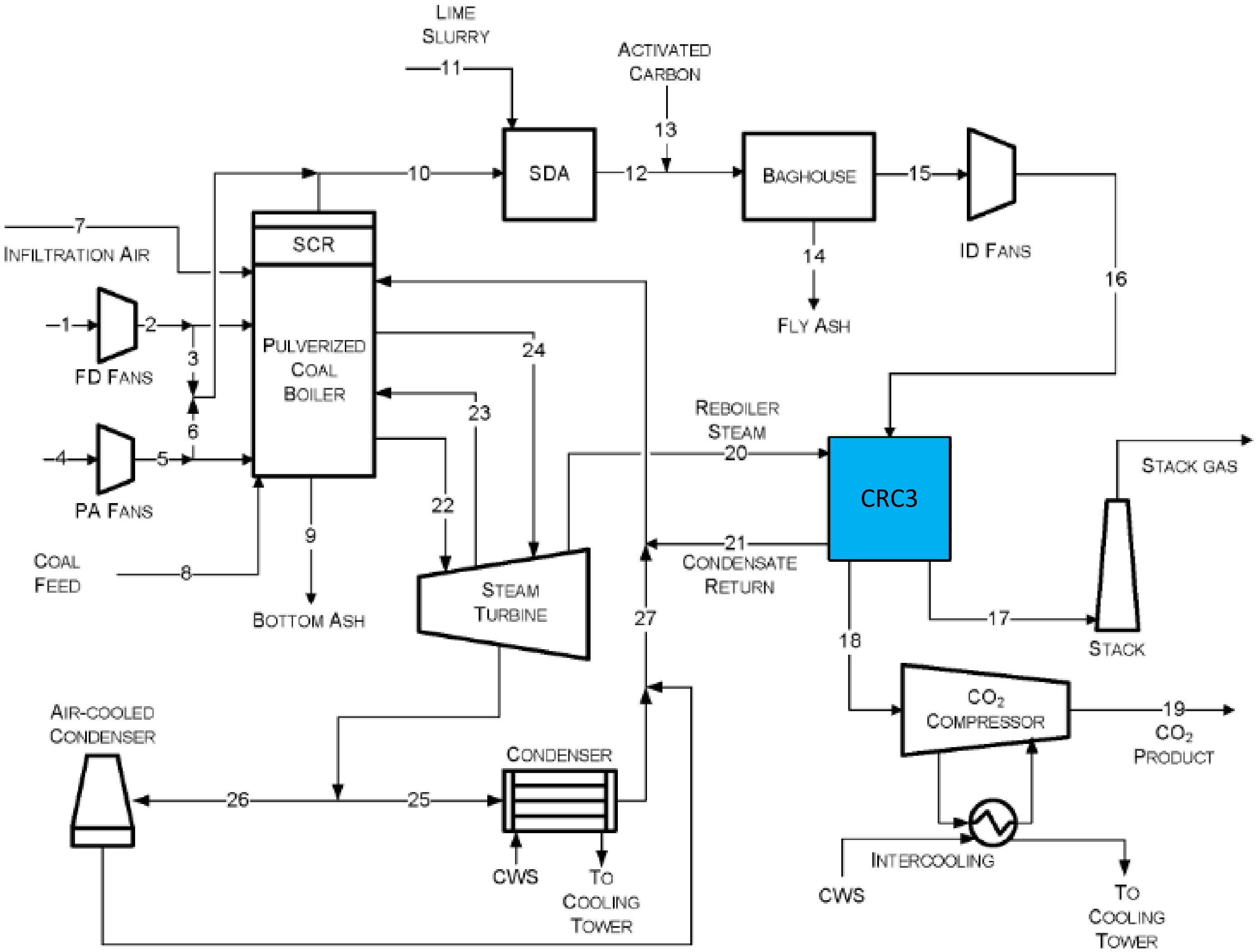

Figure 4: Process concept for the CRC3 system.

Within this post-combustion capture context, current work is targeting better process approaches to integrate heat of sorption with the heat of desorption and to further improve sorbent performance, all of which are intended to reduce capture costs and enable the commercial potential of this technology.

technology advantages

- The CRC3 approach of applying sorbent to the high surface area, wash-coated minichannel reactor walls enables indirect heating and cooling of the sorbent.
- The sorbent on the minichannel reactor walls remains fixed in place and is not subject to particle attrition resulting from particle-particle contact, as would occur in a fluidized bed.

- The dispersion of sorbent over the high surface area of the walls of the minichannel reactor enables high mass-transfer rate of CO_2 to the sorbent.
- The pressure drop through the minichannel reactor can be reduced relative to a packed-bed absorber, much in the same way that monolith-supported catalysts reduce the pressure drop in selective catalytic reactors (SCRs) and, more commonly, in automobile catalytic converters. This will enable ITAPS to handle high gas-flow rates.
- The CO_2 MBSs developed by PSU exhibit high capacity and operate at low-desorption temperatures and with lower heat of sorption, requiring less parasitic energy draw and thereby boosting plant net efficiency.
- The MBSs are engineered with specific chemical surface functionality, which allows for high CO_2 sorption capacities in high-humidity conditions.
- Sorbent performance and the CRC3 approach enable lower round-trip energy costs for a complete sorption-desorption cycle.
- Enabling the production of CRC3 reactors at low cost and integrating a carbon capture system with existing unit operations should result in lower capital and operating costs for CO_2 capture from coal-fired power plants.

R&D challenges

- Operation at lower CO_2 partial pressures in flue gas as compared to syngas used in Phase I and Phase II.
- Implementing sorbent on both sides of the contactor and coordinating heat transfer between them.
- Operating with real flue gas.

status

Project Phase I and Phase II have been completed, in which ITAPS technology was developed and feasibility demonstrated for pre-combustion capture. Phase IIB is underway, in which the MBSs integrated in microchannel heat exchangers are being improved, evaluated, and tested for post-combustion capture from flue gas.

available reports/technical papers/presentations

N/A.

Novel Process that Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process

primary project goal

The Georgia Institute of Technology developed prototype fiber sorbent modules containing polymeric fibers embedded with metal organic framework (MOF) for use in a sub-ambient rapid-cycle pressure swing adsorption (RCPSA) post-combustion carbon capture process.

technical goals

- Scaled-up the MOF sorbent.
- Experimentally determined sub-ambient sorption isotherms.
- Spun fibers containing the MOF.
- Constructed the RCPSA system and completed testing of fiber sorbent modules and fiber sorbent modules with phase-change materials.
- Modeled and optimized fiber module operation, as well as flue gas conditioning optimization.
- Prepared an overall system techno-economic analysis (TEA).

technical content

Georgia Tech Research Corporation developed a process to achieve 10 mole/kg sorbent swing capacity using an RCPSA process. The sorbent system included novel polymeric fibers embedded at high loadings with MOF materials. An example of the fibers is shown in Figure 1. MOFs are known to have good carbon dioxide (CO_2) capacity and rapid adsorption/desorption kinetics if kept isothermal. The team developed a scalable, modular contactor for the sorbents with high surface area, low pressure drop, and low mass transfer resistance. An encapsulated, stationary phase-change material was incorporated in the hollow fiber sorbents (Figure 2) to maintain isothermal adsorption/desorption. This material has a melting/freezing point equivalent to the system operating temperature. It melts as heat is released upon CO_2 adsorption and freezes as CO_2 is desorbed; therefore, steam and cooling water are not necessary. The system consists of modules containing the hollow fibers.

program area:

Point Source Capture

ending scale:

Bench Scale

application:

Post-combustion Power Generation PSC

key technology:

Sorbents

project focus:

Pressure Swing Adsorption Process with Novel Sorbent Structured Contactors

participant:

Georgia Tech Research Corporation

project number:

FE0026433

predecessor projects:

N/A

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Inmondo Tech, Inc.

start date:

10.01.2015

percent complete:

100%

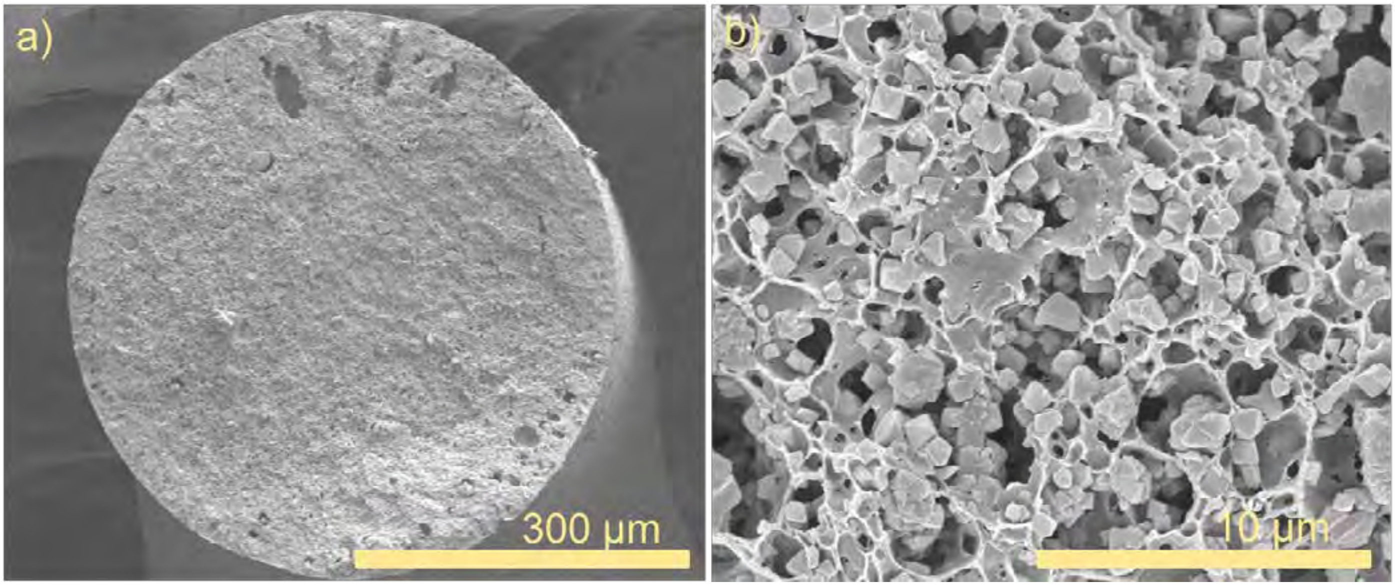

Figure 1: MIL-101(Cr)/cellulose acetate fiber sorbents: ~50 wt% MIL-101(Cr); (a) low magnification fiber, (b) zoomed in sub-structure.

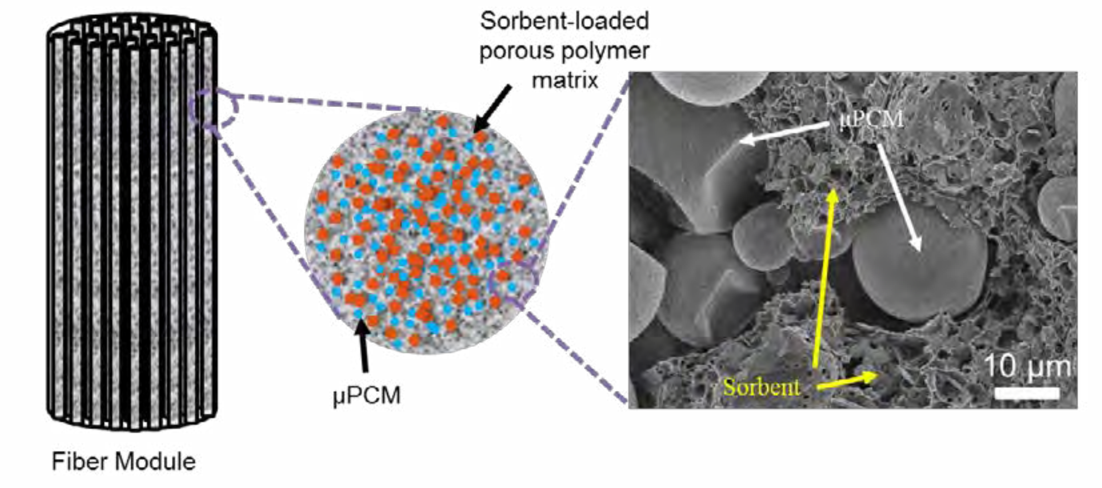

Figure 2: Phase-change material in hollow fiber sorbents.

A simplified schematic of the overall CO_2 capture process is shown in Figure 3. The conditioned flue gas is passed through a sub-ambient heat exchanger before entering the PSA unit containing the hollow fiber sorbent modules. The steps of the RCPSA process (pressurization, adsorption, depressurization, desorption) are shown in Figure 4. Sub-ambient conditions increase adsorption selectivity and working capacity.

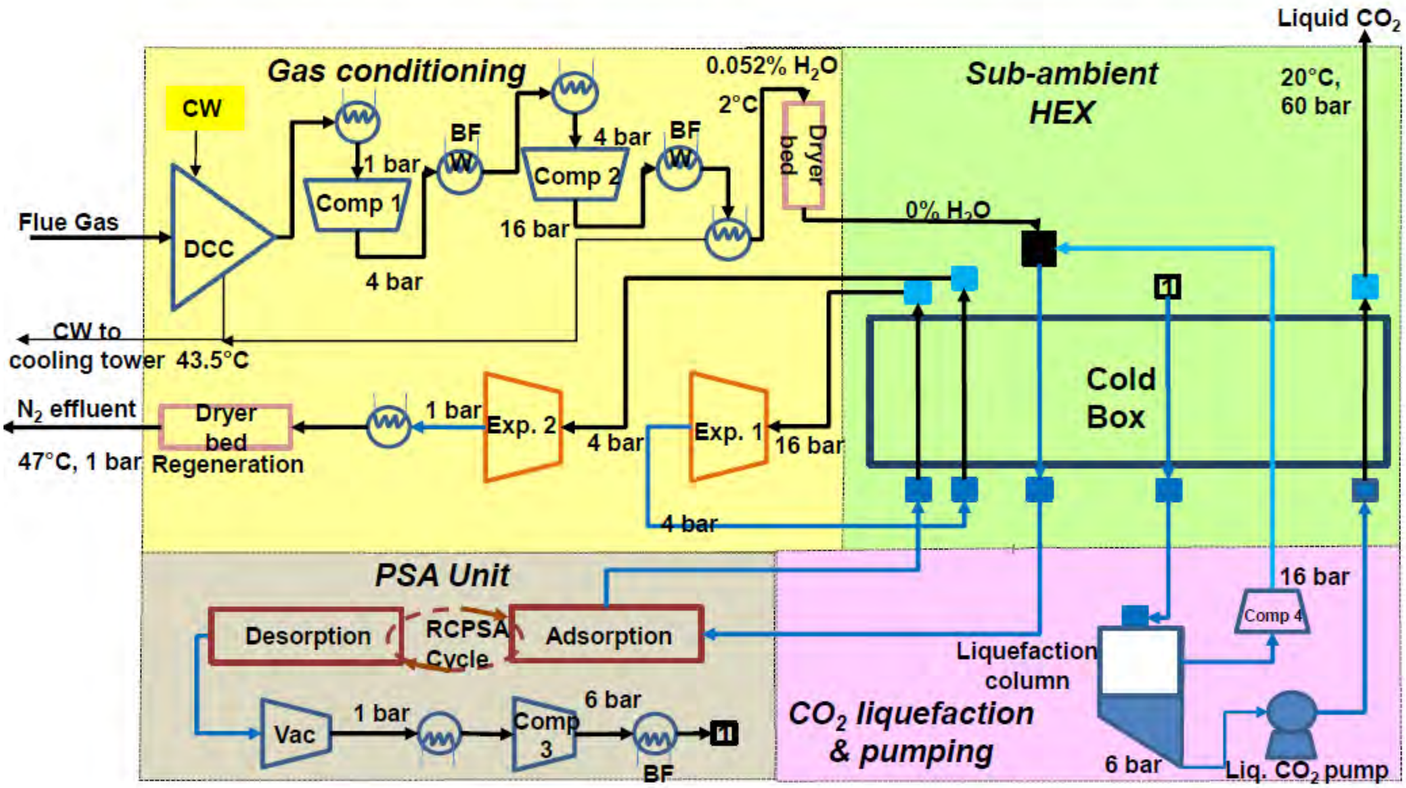

Figure 3: Process flow diagram.

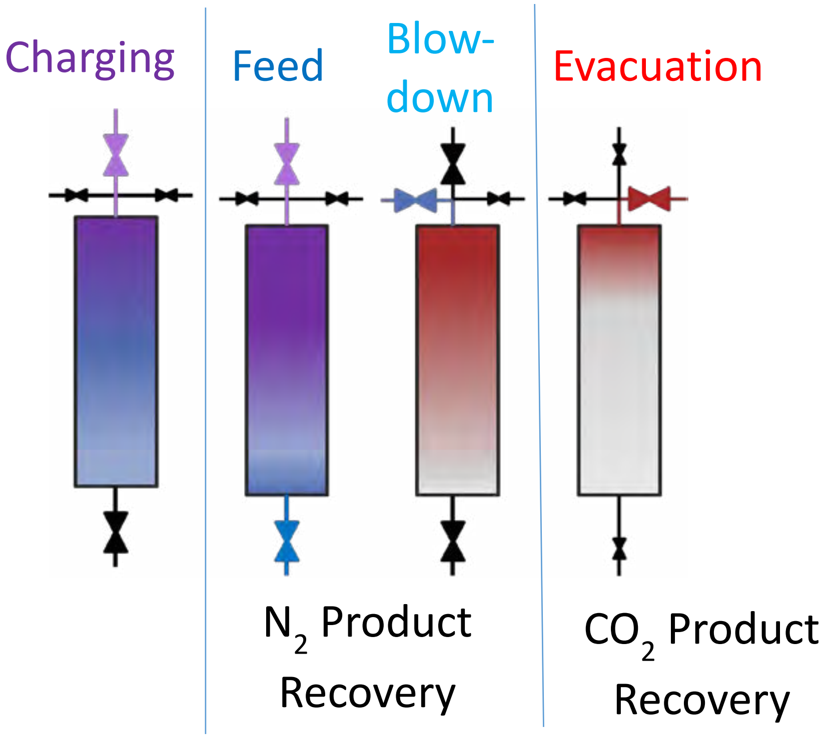

Figure 4: Pressure swing adsorption process.

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	1,200	1,200
Average Particle Diameter (diameter of fiber)	mm	0.8	0.8
Particle Void Fraction (void fraction of the fiber bed)	m^3/m^3	0.4	0.35
Packing Density	m^2/m^3	1,000	2,000
Solid Heat Capacity @ STP	kJ/kg-K	1,600	1,600
Crush Strength	kg$_f$	unknown	not specified
Manufacturing Cost for Sorbent	\$/kg	unknown	30
Adsorption			
Pressure	bar	2	2
Temperature	°C	-30	-30
Equilibrium Loading	g mol CO_2/kg	10.2	delta (ads-des) =10
Heat of Desorption	kJ/mol CO_2	21.5	< 35
Desorption			
Pressure	bar	0.3	0.3
Temperature	°C	-30	-30
Equilibrium CO_2 Loading	g mol CO_2/kg	1.2	Delta (ads-des) =10
Heat of Adsorption	kJ/mol CO_2	21.5	< 35
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed fiber/parallel flow/cyclic	
Flue Gas Flowrate	kg/hr	—	
PSA CO_2 Recovery, Purity, and Pressure [from PSA] (from total process)	%/%/bar	[92/80/1] (90/99.5/60)	[92/95/1] (90/99.9/60)
Adsorber Pressure Drop	bar	0.1	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	390-480 (process)	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High, resistant to humid sulfur dioxide (SO_2) at 50 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – Irreversible sorption of SO_2 and nitrogen dioxide (NO_2) with little effect on CO_2 capacity.

Flue Gas Pretreatment Requirements – Pressurization, dehydration, cooling.

Sorbent Makeup Requirements – None.

Waste Streams Generated – Clean (100% RH) nitrogen (N_2).

Process Design Concept – Discussed above.

technology advantages

- High working capacity of MOF sorbents.
- High contact area, low pressure drop, and low mass transfer resistance for the modules.
- Sub-ambient conditions increase adsorption selectivity and working capacity.
- The efficiency of the pressure swing cycle was boosted by installing a stationary phase-change material in the fiber sorbents that isothermally melts upon release of sorption enthalpy and conversely isothermally freezes upon CO_2 desorption, requiring no steam or cooling water.
- Improved performance in the presence of flue gas contaminants due to physisorption separation mechanism (as opposed to a chemisorption mechanism).
- Carbon dioxide liquefaction and pumping can be used instead of CO_2 compression.
- Sub-ambient heat exchange and CO_2 liquefaction are commercially demonstrated.

R&D challenges

- Scale-up of MOFs.
- Integrating MOF into the fiber to maintain CO_2 capacity.
- Integration of phase-change material into MOF-loaded fibers to maintain near isothermal operation.

- Effective operation of tightly heat- and work-integrated system.
- Monitoring and management of sorbent lifetime over extended operating periods.
- Simulation development for material screening, adsorption process selection, and cost estimation.

status

The project was completed on September 30, 2019. Two MOFs were manufactured in large quantities and subsequently converted into adsorbent-loaded fiber materials. These were shown to have more than order-of-magnitude reductions in flue gas pressure drop compared to traditional adsorbent structures. The MOF materials could be composited with glycol-loaded capsules that would freeze and melt during each sorption-desorption cycle, enabling near isothermal operation of the RCPSA. Two mini pilot systems were constructed for testing, and a multi-level simulation for capture mechanisms, thermodynamics, and process-level integration was developed for systems of this technology type. The sub-ambient RCPSA process was estimated to have competitive operating and capital costs via a preliminary TEA based on the experimental data and computational modeling at molecular and process levels.

available reports/technical papers/presentations

Lively, R., et al. “Novel Process That Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process,” Presented at the Final Project Meeting, Pittsburgh, PA, September 2019. *https://netl.doe.gov/sites/default/files/netl-file/R-Lively-GIT-Rapid-Pressure-Swing.pdf*.

Lively, R., et al. “Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption,” presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/netl-file/K-Walton-GIT-10-MOL-per-KG-Swing-Capacity.pdf*.

Lively, R., et al. “Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption,” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/R-Lively-GIT-10-MOLKG-Sorbent-Swing-Capacity.pdf*.

Lively, R., et al. “Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-Ambient Pressure Swing Adsorption,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/R-Lively-GeorgiaIT-Sub-ambient-Pressure-Swing-Adsorption.pdf.*

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Park, J., et al. “Establishing upper bounds on CO_2 swing capacity in sub-ambient pressure swing adsorption via molecular simulation of metal–organic frameworks” J. Mater. Chem. A, 2017, 5, 12258-12265.

Park, J., et al. “How Reproducible Are Isotherm Measurements in Metal–Organic Frameworks?” Chem. Mater., 2017, 29, 24, 10487–10495.

Park, J. et al. “*How Well Do Approximate Models of Adsorption-Based CO_2 Capture Processes Predict Results of Detailed Process Models?*” Ind. Eng. Chem. Res. 2020, 59, 15, 7097-7108

Shih, C., J. Park, et al. “*Hierarchical Bayesian estimation for adsorption isotherm parameter determination” Chem. Eng. Sci. 2020, 2014, 115435*

DeWitt, SJA, et al. “*Development of Phase-Change-Based Thermally Modulated Fiber Sorbents*” Ind. Eng. Chem. Res. 2019, 58, 155, 768-5776.

DeWitt, SJA, et al. “*Analysis of energetics and economics of sub-ambient hybrid post-combustion carbon dioxide capture*.” AIChE J. 2021, 67, 11, e.17403

DeWitt, SJA, et al. “*Critical Comparison of Structured Contactors for Adsorption-Based Gas Separations” Annu*. Rev. Chem. Biomol. Eng. 2018 Jun 7;9:129-152.

DeWitt, SJA et al. “*Incorporation of microencapsulated phase change materials into wet-spin dry jet polymer fibers.*” PCT US18/48110; WO 2019/099086.

Process for CO_2 Capture from Low-Concentration Sources

primary project goal

InnoSepra LLC has developed a low-cost capture process using structured sorbents to remove carbon dioxide (CO_2) from low-concentration feed streams. The project demonstrated the technical and economic feasibility of using structured sorbents for CO_2 capture in InnoSepra's novel adsorption-based process through lab testing, process modeling and simulation, and a detailed techno-economic analysis (TEA). Physical sorbents in their structured form have significantly lower pressure drop, require less parasitic power and plot area, and have a lower overall capital cost compared to their particulate counterparts. Laboratory tests indicated that these physical sorbents can remove moisture and concentrate CO_2 from low-concentration sources at a very high efficiency and require low parasitic power.

technical goals

- Fabricate adsorption test modules for CO_2 and moisture adsorption.
- Complete semi-bench-scale testing for moisture removal.
- Complete lab- and semi-bench-scale testing for CO_2 adsorption.
- Perform an engineering design for CO_2 enrichment of the residue stream for a 550-megawatt-electric (MWe) power plant.
- Prepare a TEA for a feed plant of 1 million standard cubic feet per minute (scfm).

technical content

InnoSepra developed a process, as shown in the schematic in Figure 1, using structured sorbents to capture CO_2 from low-concentration sources, which minimizes the pressure drop for the very high flows associated with the low-concentration sources. For a dry residue stream, a single-stage process is utilized to remove CO_2 with the structured sorbents. To treat a wet residue stream, a two-stage process is employed. Moisture is removed in the first stage in a rapid cycle adsorption process. The CO_2 adsorption occurs in the second stage, using the structured sorbents in an adsorption process. This stage produces a CO_2-enriched stream containing 10–15% CO_2 after regeneration, which can be fed to a new or an existing post-combustion CO_2 capture system. The structured sorbents used in this process have very high capacities at low-CO_2 concentrations and can be regenerated to produce the CO_2-enriched stream, achieving a CO_2 enrichment by a factor of five to 10.

Phase I focused on lab-scale evaluation of prototype adsorbents using low-CO_2 concentration simulated feed gas. Phase II included fabrication of test modules and evaluation of the structured sorbents for moisture removal and CO_2 adsorption capacity. Test unit modules were evaluated in two different configurations: a rotating-bed configuration and a fixed-bed configuration. Test results inform parameters needed for an engineering design of a full-scale plant and for a TEA.

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Structured Sorbent-Based Process for Low CO_2 Concentration Sources

participant:
InnoSepra LLC

project number:
SC0015114

predecessor projects:
N/A

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partners:
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start date:
02.22.2016

percent complete:
100%

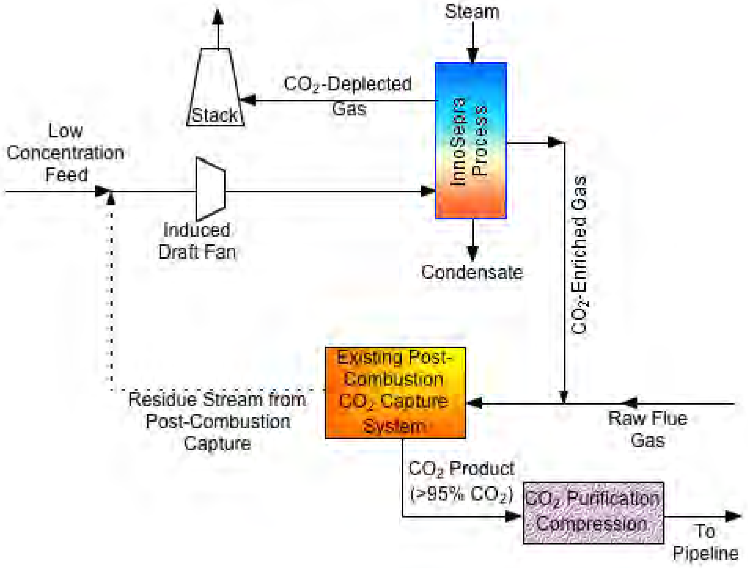

Figure 1: InnoSepra capture process.

technology advantages

The structured sorbents have:

- A very high surface area-to-volume ratio and a lower heat requirement for regeneration compared to amine-based absorption using structured packing.
- Are not subject to fluidization constraints or attrition concerns.
- Very low pressure drops, typically 1/5–1/10th of particulate adsorbents.
- Very small effective particle size (less than 80 µm) that provides very short mass transfer zones.
- Ability to process significantly higher flows for a given bed volume compared to particulate adsorbents, which is particularly beneficial for low-concentration source CO_2 capture where flow rates can be much higher.
- Ability to be fabricated using virtually any commercially available adsorbent.

R&D challenges

- Assuring sufficient moisture removal to enable significantly higher CO_2 capacity for the sorbent in the CO_2 adsorption stage.
- Validating the process model with test results.

status

Process economic evaluation based on the experimental data, process modeling, and scale-up studies indicated that the structured sorbents can cost-effectively concentrate CO_2 from a stream containing 1–1.5% CO_2 (typical of a residue stream after 90% CO_2 capture from a supercritical pulverized coal post-combustion capture process) by a factor of 10 or more. The CO_2 enrichment cost depends on the moisture content of the residue stream. If the residue stream is moisture-saturated (such as that from an amine-based capture process), the enrichment cost is about $55/tonne. If the residue stream is nearly dry (such as that from InnoSepra's adsorption-based post-combustion CO_2 capture process), the enrichment cost is about $37/tonne. The original project milestones, both in terms of process performance and the CO_2 capture cost, were significantly exceeded during the execution of this project. The current CO_2 enrichment costs of $37–55/tonne are significantly better than a cost of $350/tonne for the amine-based process for low-concentration streams. If the enriched CO_2 stream is mixed with the feed to a post-combustion CO_2 capture process, cost-effective capture of 98–99% of CO_2 is possible. The results from this project are also applicable to CO_2 capture from a natural gas combined cycle (NGCC) plant and may eventually allow CO_2 capture from air at a cost of $110–150/tonne. If the captured CO_2 is used for enhanced oil recovery (EOR), it can potentially address, depending on the oil price, a CO_2-EOR market worth more than $100 billion without the need for climate legislation. EOR can also store up to 30 gigatons (equivalent to emissions from 140 gigawatts of coal-based power generation for 35 years) of CO_2 in oil fields, significantly reducing the carbon footprint of coal-based power generation and oil production.

available reports/technical papers/presentations

Jain, R. “Process for CO_2 Capture from Low Concentration Streams,” Final Technical Report, August 2018. *https://www.osti.gov/biblio/1577323-process-co2-capture-from-low-concentration-sources*.

Jain, R. “Process for CO_2 Capture from Low Concentration Streams,” presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/R-Jain-InnoSepra-Low-Concentration-Capture.pdf*

Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing

primary project goal

ION Clean Energy Inc. (ION), formerly ION Engineering LLC, developed advanced gas-liquid contacting devices that enable more efficient capture of carbon dioxide (CO_2) with reduced process footprints. The Modular Adaptive Packing (MAP) design incorporates a mathematically driven model for creating a contacting device built for integrated mass transfer and heat transfer based on computational fluid dynamics (CFD). The overall objective of this project was to design, fabricate, and evaluate packing internals in a packing characterization rig.

technical goals

- Design MAP modules for testing at ION's pilot facility.
- Use 3D-printing techniques to fabricate MAP modules in plastic for design verification, including but not limited to fit, performance, and stress testing.
- Use 3D-printing techniques to fabricate metal MAP module prototypes for packing characterization.
- Modify ION's capture rig to a packing characterization rig for suitable evaluation of packings regarding pressure drop, active surface area, and liquid hold-up measurements.
- Perform baseline testing in the modified rig using commercially available packing.
- Install the 3D-printed metal MAP modules into the packing characterization rig and perform systematic testing to verify packing design performance.
- Incorporate experimental test results into process models and perform simulations on new structured packings.
- Implement simplified packing models that are descriptive of the MAP with monoethanolamine (MEA) in the acid-gas software modeler, ProTreat®, for further data analysis and concept evaluation.

technical content

Standard CO_2 absorption technologies create heat (i.e., exothermic) upon reacting CO_2 with a liquid absorbent. When optimizing for process efficiency, the greatest amount of heat released occurs toward the top of the absorber in close proximity to the clean flue gas exit, and as such, carries the risk of solvent loss through evaporation at an elevated temperature. Therefore, the project described herein

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Novel Concepts

project focus:
Advanced Gas-Liquid Contacting Devices for CO_2 Capture

participant:
ION Clean Energy Inc.

project number:
FE0031530

predecessor project:
SC0012056

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start date:
01.19.2018

percent complete:
100%

addresses the challenges of internal gas-liquid contactors and novel methods for controlling evaporative solvent loss risks.

The internals of process columns (e.g., distributors, packing, and collectors), heat exchangers, and emissions control measures are among the highest capital costs in CO_2 capture plants. ION's MAP technology provides a way to lower the cost of column internals in CO_2 capture systems, while simultaneously reducing degradation rates and emissions of typical amine-based capture solvents, thereby allowing for more economically sustainable capture plant operations. The use of 3D printing to fabricate packing internals reduces the costs, which allows for the total freedom of design of the gas-liquid interaction area and the complete integration of intra-column cooling. 3D printing is an "additive" fabrication technique that offers unprecedented advantages in accelerating the design cycles of gas-liquid contacting devices, minimizing manufacturing costs, and expediting the deployment timeline for CO_2 capture commercially.

Through the use of 3D printing, ION can maximize the surface area to void volume of the contactor surface through complete geometric freedom. The flow domain consists of a cylindrical tube that encapsulates a hollow structure. The hollow structure forms a network of channels filled with cooling water, where CO_2-containing air and liquid absorbent can chemically react in the space outside the cooling water channels for heat transfer. The design essentially combines the absorber gas-liquid contactor with an in situ heat exchanger.

This project was a continuation of a previous U.S. Department of Energy (DOE)-funded Small Business Innovation Research (SBIR) project, DE-SC0012056. Phase I results of the SBIR project showed that the mass transfer increases with increasing surface area-to-volume ratios in the packing. In Phase II, ION developed a dual-function mass and heat transfer packing medium to incorporate heat transfer into the design. The design team first 3D-printed plastic prototypes to test for overall fit, check for design flaws, and evaluate the potential for commercialization. ION engineers landed with a final design using metal and then tested in ION's 1-kilowatt-electric (kWe) lab pilot (Figure 1) CO_2 capture unit using a common benchmark solvent of 30 wt% MEA and synthetic flue gas. The results were compared to commercially available and optimized structure packing (Sulzer Mellapak 350X) tested in the same unit under the same process conditions. The results of the testing showed more than a 10°C reduction in absorber maximum temperature compared to baseline structured packing, which leads to significantly reduced emissions. Additionally, the mass transfer was comparable and within 5% of the benchmark results. As expected, the MAP was shown to have inferior pressure drop properties, mainly due to the addition of cooling channels. Other contributing factors to the increased pressure drop were the internal support structures within the additive packing, which were necessitated by the metal printing process and had to be added to the design prior to printing. However, when cooling was implemented, the pressure drop was lower (~15%) compared to the uncooled version. At a larger scale, important for commercial viability, the pressure drop will decrease since a much lower volume fraction will be occupied by the cooling channel and its wall thicknesses. Also during Phase II, ION designed a CFD model to simulate the CO_2 capture process. The model predicted the flow and energy dynamics of coolant water, the gas flow, and the distribution of liquid solvent in the domain, as well as the CO_2 absorption for a various geometries and operating conditions. CFD lends itself to parameterization—wherein geometry, flow rates, and other tunable variables, such as the reaction mechanism and rate, can be changed to understand the entire design space available and optimize the model before the fabrication of prototypes. Figure 2 shows a computer model and the resulting plastic and metal printed prototypes. Overall, the SBIR project successfully demonstrated the commercial viability of customizable and modular packing devices that incorporate both heat and mass transfer for CO_2 capture and other applications where exothermic reactions are involved.

Figure 1: ION's lab-pilot (0.001 MWe) CO_2 capture test unit.

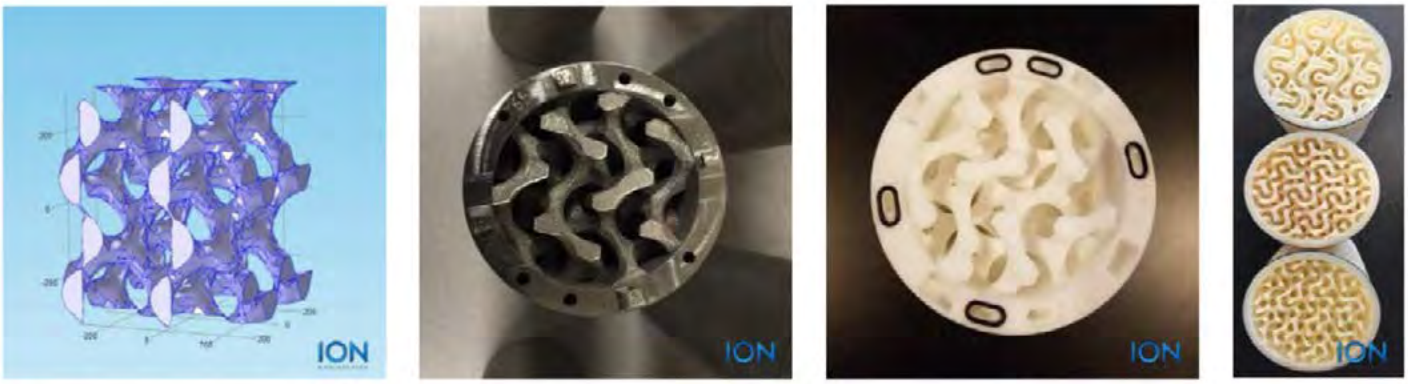

Figure 2: Design model, metal prototype, and plastic prototypes from SC0012056.

This Phase III project consisted of advanced manufacturing efforts that resulted in a 3D-printed commercial prototype of a gas-liquid contacting device that is modular and adaptable to both small- and large-scale applications. Further enhancements were made to the heat exchange, which allowed for further improved mass transfer and a significant decrease in pressure drop. ION utilized the design work from the previous SBIR project and incorporated expertise from commercial experts such as ANSYS and 3D Systems to produce an optimized MAP prototype design. Design parameters were evaluated, including the shape of inner walls and structures to promote primary and secondary mixing, liquid-gas mass transfer contact area, liquid-liquid heat exchange area, wall thickness and integrity, material choice, and the ratio of area for gas and liquid flow versus coolant flow. These design parameters were evaluated across a range of process parameters, such as pressure drop, mass and heat transfer between gas and liquid phases, heat transfer between cooling or heating medium and liquid-gas channel, heat transport within a module and within a range of modules, and connectivity, and also provided safeguards in the event of leakage, wall-effects, entrainment, and flooding. Design strategies focused on three areas of optimization using computational analyses:

- Heat transfer by liquid flow design (using CFD modeling), inlet and outlet positioning, material choice, and vanes.
- Specific area by vanes and printing surface roughness.
- Pressure drop on the gas side:
    - The incorporation of aerodynamic principles and circumvent channeling.
    - The incorporation of considerations on gas volumetric flow changes throughout packing (temperature, CO_2 removal).

Prototypes were printed in plastic using a stereolithographic apparatus for design and structural verification and metal prototypes were printed based on the final design. MAP modules were successfully fabricated at 10-inch diameter and 12-inch height (Figure 3) and stacked to create a packed column of 12-feet height. These modules were tested in ION’s packing characterization rig that was modified to accommodate the MAP modules, as well as a standard column that incorporated a commercial-structured packing. The packing characterization rig with MAP is shown in Figure 4. The characterization provided empirically determined packing characteristics, including pressure drop over the height of the packing as a function of gas- and liquid-load and viscosity; packed-bed liquid holdup over a broad range of column gas and liquid loads; and effective surface area of the packings as a function of gas and liquid load. The packing bed pressure drop and liquid holdup were measured at two viscosities (using air/water and air/water/glycerin mixtures). The mass transfer and hydraulics of MAP, with intracooled channels, showed similar trends to that of the Sulzer commercial packing (Mellapak250Y). However, at both fluid viscosities, pressure drop results were observed to be lower for MP250Y compared to MAP, due to the higher void space in the Sulzer packing, which does not contain internal channels for cooling. The column packing's effective surface area was measured using an aqueous solution made up of 0.1 M sodium hydroxide and ambient air as the gas phase. The MAP showed excellent wetting and liquid distribution, with an effective area reaching 100% of the theoretical area at high wetted rates. Experimental results on the MAP were 107 m^2/m^3 for the highest liquid flow, a wetting coverage of 93%.

Figure 3: 3D-printed columns in plastic and metal.

Figure 4: ION packing characterization rig with MAP.

In summary, although the uncooled MAP has a higher pressure drop than MP250Y, adding intracooling reduced the overall column pressure drop of MAP to below the pressure drop of MP250Y. Intracooling lowers pressure drop in the column due to two effects:

- Higher intracooling results in lower solvent flow rates, which reduces liquid holdup and overall pressure drop.
- Higher intracooling decreases gas temperature, which reduces superficial gas velocity and overall pressure drop.

Thus, the intracooled column outperforms an adiabatic absorber in all cases.

While the absorber modeling work done for the MAP analysis used the industry standard 30 wt% MEA solvent, intracooling can have a large impact on the performance of all advanced solvents. By dropping the solvent circulation rate at critical lean loadings up to 30%, many of the pumps, heat exchangers, and regenerator equipment may be significantly smaller. Previous work has shown that an optimized intercooling section can drop overall cost of capture for the advanced piperazine solvent by \$1.70/tonne CO_2 when balancing increased cost for absorber internals with decreased cost in regeneration (Frailie, 2014). Potential savings with intracooling (such as the elimination of solvent collection/distribution trays) may result in an additional 10% savings (to \$1.87/tonne CO_2) when compared to simple intercooling. Higher heat removal in the absorber (22%) and solvent CO_2 carrying capacity gains (4%) represent further savings. In addition, ION anticipates a decrease in solvent losses at lower absorber operating temperatures. Future additive manufacturing costs must fall as the module dimensional scaleup increases before significant potential savings from intracooling could be fully realized with MAP for large-scale carbon capture facilities.

technology advantages

- Eventually, lower cost of column internals, including distributors, packing, and collectors.
- Reduces degradation rates and emissions of typical amine-based capture solvents.
- Modular and scalable, which allows for customization of temperature profiles, mass transfer, and pressure drop.
- The use of 3D printing allows for the use of lower-cost materials and minimizes manufacturing costs.

- It allows for control of absorber profile temperatures, which leads to reduced emissions-related issues and lower energy consumption. This allows for significant capital savings in the water wash by reducing packing height requirements and results in lower operating expenses due to reduced solvent makeup.
- The rapid and flexible feedback loop between design, fabrication, and testing provided through 3D printing advances the performance and lowers the costs of gas-liquid contacting devices for CO_2 capture.
- The intracooled section can have built-in redistributors, simplifying column design compared to traditional intercooling that needs draw-off trays and distributors above and below the intercooling point.

R&D challenges

- Reducing additive manufacturing costs as the modules are scaled-up to allow for significant potential savings from intracooling when applying MAP to large-scale carbon capture facilities.

status

The project was completed in November 2020. ION Clean Energy Inc. (formerly ION Engineering LLC) tested a standard Mellapak 250.Y packing and ION's MAP packing in their packing characterization rig. The hydraulics, mass transfer, and heat transfer of the MAP offer an ideal solution for mitigating the CO_2 absorption exotherm for MEA. Future research toward commercialization includes scaling-up the size of a 3D-printed module, decreasing the cost of 3D printing, and designing MAP interconnections for multiple modules in a single layer.

available reports/technical papers/presentations

Meuleman, E., Panaccione, C., Atcheson, J., Silverman, T., and Staab, G., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," presented at the 2020 Carbon Capture Integrated Project Review Meeting, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Fine.pdf*.

Meuleman, E., Panaccione, C., Atcheson, J., Silverman, T., and Staab, G., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Meuleman-ION-Novel-Contacting-Devices.pdf*.

Meuleman, E., Atcheson, J., and Panaccione, C., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/E-Meuleman-ION-Rapid-Design-and-Testing-of-Contacting-Devices.pdf*.

Meuleman, E., Atcheson, J., and Panaccione, C., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," Project Kickoff Meeting. July 2018.

Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications

primary project goal

LumiShield Technologies is developing and demonstrating durable and inexpensive anti-corrosion coatings for application on carbon steel, which is used extensively in vessels and piping of power plant boilers and capture systems. By reducing corrosion and allowing substitution of coated mild or carbon steel for expensive stainless steel, capital costs of power plant systems could be significantly reduced, helping to enable cost-effective carbon dioxide (CO_2) capture for coal- and natural gas-fired power generation.

The multi-layer coating structure consists of a novel mixed metal oxide coat covered with an organic anti-corrosion coating. Project objectives are initially focusing on optimizing the metal oxide base layer for applying the organic coatings and proving the effectiveness of a prototype two-layer coating in preventing corrosion. Subsequently, the objectives are for optimization through identification of the organic coatings that give the best performance in combination with the optimized metal oxide base layer and showing the economic advantage of using the coatings through cost-benefit analysis.

technical goals

- Improve the corrosion resistance of organically coated steel (by at least 10% in terms of higher salt spray hours) by addition of the LumiShield metal oxide base coat underneath the conventional organic top coat.
- Perform lab-scale testing of LumiShield-coated carbon steel samples in simulated amine capture system conditions (CO_2 saturated 30% monoethanolamine [MEA] solution at 60ºC) and realistic flue gas conditions.
- Optimize top-coating chemistry to maximize adhesion to LumiShield aluminum oxide coating under exposure to acids and amines, as evidenced by no change in appearance or adhesion, including blistering or swelling of organic coatings under realistic testing/exposure conditions.
- Provide a cost-benefit analysis for completed composites and compare with existing coatings and materials, making quantified estimates of: (1) how much stainless steel is replaceable by carbon steel with LumiShield coating in a baseline system, and (2) savings in capital and operating costs for the baseline system (with the quantitative target that at least one of the coatings should result in a decrease in cost per tonne of CO_2 by 1% or greater).

technical content

In fabrication of piping and vessels in power plants, carbon steel is the preferred material of construction given its relatively high strength and relatively low cost. However, in applications for corrosive environments (e.g., acid gas-containing flue gas streams, amine solutions in capture systems, and wet CO_2 captured by amine systems), carbon steel may not provide suitable corrosion resistance. Stainless steel provides high corrosion resistance, but it is expensive. Conventional organic-

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Enabling Technologies

project focus:
Corrosion-Resistant Coated Carbon Steel Components

participant:
LumiShield Technologies Inc.

project number:
FE0031659

predecessor projects:
N/A

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partners:
N/A

start date:
10.01.2018

percent complete:
100%

coated steel initially confers corrosion resistance but tends to develop defects though which diffusion of water and gas species can occur, leading to corrosion of the substrate and delamination of the coating (as illustrated in Figure 1). Therefore, better anti-corrosion coatings are needed in applications such as corrosive solvent-containing carbon capture systems.

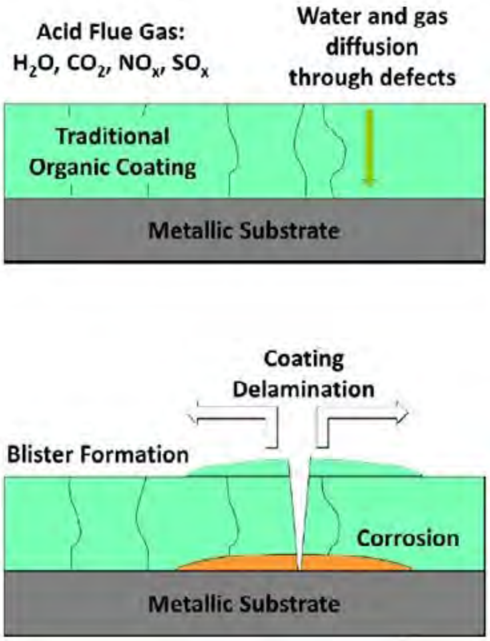


Figure 1: Mechanism for corrosion of coated metallic substrates.

The approach to this problem involves utilization of previously developed LumiShield metal oxide coating technology to establish a base metal oxide layer on carbon steel, on which organic coatings tailored for resistance to amine solutions could be applied. The basic geometry of the dual coating concept is depicted in Figure 2. The presence of the LumiShield coating improves the adhesion of the organic coating, preventing the coating from being undermined and considerably increasing the overall coating performance. The LumiShield coating was initially developed as a stand-alone anti-corrosion coating to replace toxic metal coatings like chromium and cadmium. However, realization occurred that the metal oxide surface would allow excellent adherence of organic coating molecules and that the resulting composite coating could make use of a thinner organic layer with fewer defects, improving corrosion resistance performance and reducing cost. The metal oxide layer itself may be applied in a single step using equipment and expertise well-known to the industry. These characteristics allow competitive or even lower costs than conventional primed steel coatings, which sometimes require multiple layers at increased cost.

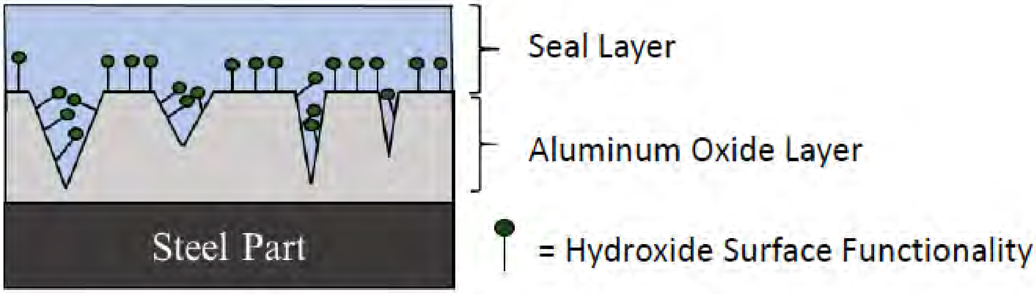


Figure 2: Coating structure.

Metal Oxide Base Layer

The metal oxide layer consists mainly of aluminum oxide applied via electroplating, utilizing water-stable aluminum complexes (with proprietary additions) in the electroplating bath, which form a coherent and highly adherent aluminum oxide layer on steel via a proprietary cathodic electroplating process. It has been observed that the aluminum oxide layer formation allows for some degree of metal-to-metal bonding between aluminum centers and the steel substrate, giving the coating excellent adhesion. The LumiShield alumina electrodeposition process takes place in an aqueous system, offering significant cost advantages over non-aqueous methods of alumina deposition that require processes to be free of atmospheric water and oxygen. The process is analogous to the electroplating of common metals like zinc and can be applied using standard equipment present in every electroplating facility.

The LumiShield approach makes use of pulse-plating methods (in which electrical field strength is varied to improve control over electroplating processes). By adopting a pulsed-plating procedure (example illustrated in Figure 3), the LumiShield coating is further improved in adhesion and density. Also, the nature of the coating process allows a large degree of control of the morphology of the coating. By adjusting the electroplating conditions of pulse, pH, temperature, and solution composition and concentrations, it is possible to create morphologies ranging from plate-like growth with a so-called cracked glass appearance under magnification (Figure 4, left side) to granular growth structures (Figure 4, right side). The cracked glass morphology is valuable because its high surface area will improve the adhesion of organic layers deposited on top of it.

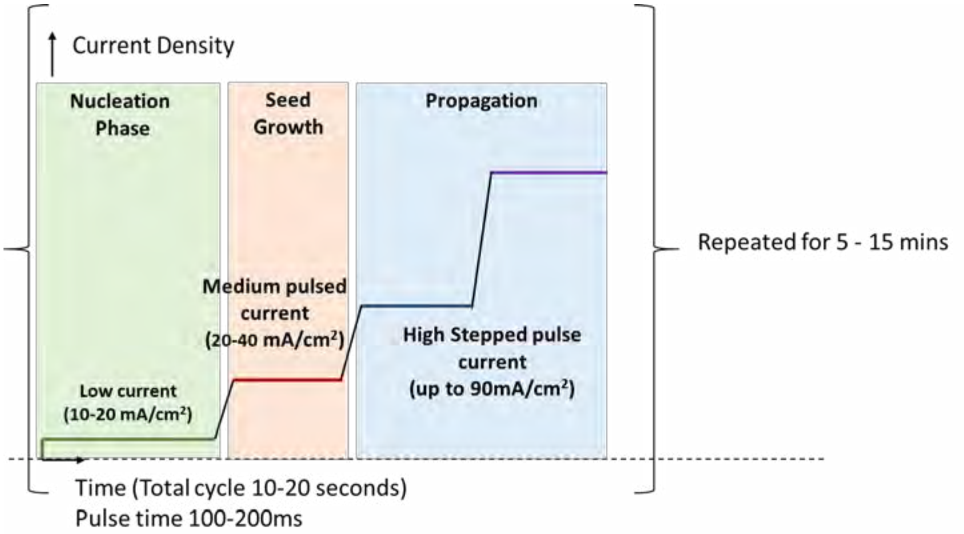


Figure 3: Complex electroplating pulse scheme.

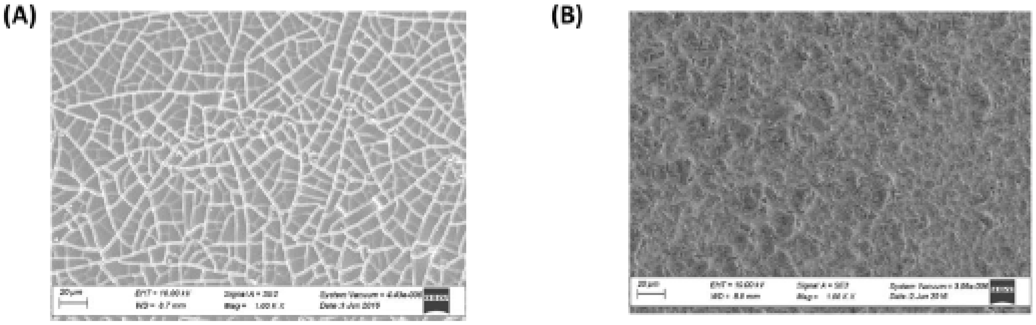
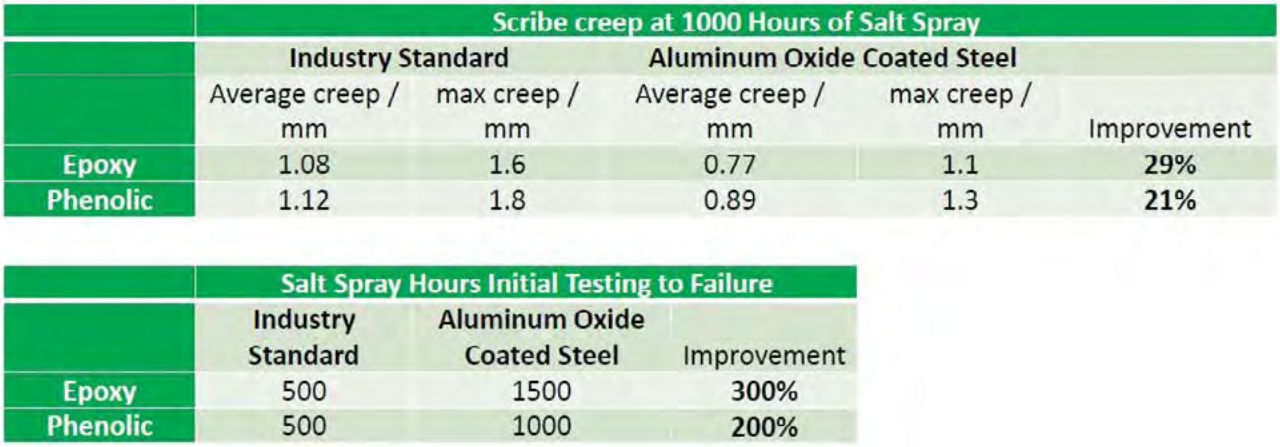


Figure 4: Variation in metal oxide coating morphology.

A major focus at the start of the project was optimization of the LumiShield metal oxide base layer. This was accomplished by varying process and electroplating solution conditions in forming the metal oxide coatings, which were then characterized for morphology and adhesion through physical and optical methods. Polarization testing to determine corrosion rates, electrochemical impedance spectroscopy to determine corrosion mechanisms, and salt spray exposure testing were conducted. LumiShield has identified plating solution parameters (temperature, pH, concentrations), as well as electrochemical process variables (pulse scheme, current density, timing), which result in thin, rough, adherent metal oxide coatings that will promote organic top-layer adhesion.

Organic Top Layer

For the essential organic top layer, LumiShield has surveyed existing/available organic anti-corrosion coating materials and identified epoxy resins, phenolic resins, and fluoropolymer resins as the three types for consideration for applications involving amine solutions, flue gas, and wet CO_2, given their formulation flexibility, robustness at elevated temperatures (as high as 180–250ºC for epoxy coatings and 120–200ºC for phenolic coatings), chemical resistance, and physical characteristics. Project work has involved testing of these three types with and without the LumiShield base coat to establish baselines for each polymer class for corrosion resistance, adhesion and scribe creep, and measure improvement of corrosion resistance in salt spray tests. Testing has shown significant improvement in corrosion performance with both epoxy and phenolic coatings, both of which likely have enhanced adhesion on the LumiShield metal oxide base layer that is improving corrosion protection. Specifically, epoxy coatings appear to be the best candidate for modification and further work to improve performance as the project progresses. On the other hand, it has been concluded that fluoropolymer coatings (which show poor adhesion to many materials) will probably not meet performance goals. Figure 5 shows interim results on these evaluations for the more promising epoxy and phenolic coating choices.



	Scribe creep at 1000 Hours of Salt Spray				
	Industry Standard		Aluminum Oxide Coated Steel		
	Average creep / mm	max creep / mm	Average creep / mm	max creep / mm	Improvement
Epoxy	1.08	1.6	0.77	1.1	**29%**
Phenolic	1.12	1.8	0.89	1.3	**21%**

	Salt Spray Hours Initial Testing to Failure		
	Industry Standard	Aluminum Oxide Coated Steel	Improvement
Epoxy	500	1500	**300%**
Phenolic	500	1000	**200%**

Figure 5: Comparisons of performance of epoxy and phenolic top coats with and without LumiShield metal oxide base coat.

To facilitate the attachment of top layer to the aluminum oxide base coating, several organic treatments have been considered based on silane treatment (silane is an inorganic compound with the chemical formula SiR_4). Silanes are used in a large variety of high-performance coatings as a binding agent between organic resins and inorganic substrates. The aim is to bind silanes to the pendant hydroxide functionality of the aluminum oxide layer (refer to Figure 2 depicting this idea) to create a synthetic handle for incorporation of the silane into the polymer top layer. To this end, several silane candidates will be investigated.

Non-Capture Applications

Although LumiShield's project focus has been application of the coatings for carbon capture systems, it has two customers that are interested in piloting LumiShield technology with specific modifications to their specific paints:

- An automotive company interested in high-temperature paint adhesion for heat shields.
- Expansion of an oil and gas program toward other markets and corrosion sites using heavy brine solutions.

There is also interest in corrosion resistance to other corrosive amines to serve the needs of the broader chemical industry.

Cost-Benefit Analysis

The LumiShield team includes AECOM, who performed a preliminary cost-benefit analysis of LumiShield's coating technology. An initial objective was to determine the highest value targets in the carbon capture system for materials replacement with the developed aluminum oxide coating over incumbent construction methods. Initial analysis has found that stainless steel currently used for fabrication of both the absorber and stripper could be replaced by LumiShield-coated mild steel with powder-coating at a capital cost saving of 13% and 17%, respectively. They also note that the replacement of stainless steel parts with mild steel may have additional nonquantifiable benefits (e.g., improved materials of construction may allow a wider range of operating conditions or allow use of amine species previously ruled out due to their effects on the stainless steel construction materials). Furthermore, cost savings might be improved significantly based on increasing part lifetime by using a new coating system.

technology advantages

- Coated mild steel can cost-effectively replace stainless steel constructions.

- Coatings can be made acid- and amine-resistant with suitable top coats.
- Coatings can be readily fabricated using straightforwardly implemented aqueous electroplating methods.
- Coatings of the type being developed are non-toxic and can replace heavy metal-based processes.
- May be used to avoid chloride stress cracking of stainless steel in some services.

R&D challenges

- Achieving a dense base metal oxide coating layer with high roughness suitable for securely attaching the upper coating layer, and the general difficulties of controlling results in utilization of electroplating methods.
- Achieving chemical and physical compatibility between the metal oxide base layer and upper organic layer.
- Attaining substantially improved performance of prototype organic coatings on the metal oxide base layer.
- Developing surface repair technique for coatings when damaged during shipping or installation.

status

LumiShield techno-economic analysis (TEA) of the fabrication of dense metal oxide-based coatings led to a 1.5% decrease in cost per tonne CO_2, and the coating predicted cost was \$0.06/ft^2. The fabricated coatings led to a 15% decrease in capital expenditure (CAPEX) for absorber and stripper. The native aluminum oxide and epoxy silane were identified as the best binder conditions. Aluminum oxides show improvement over industry standard pretreatments. The optimized dense, adherent aluminum oxide coating achieved by pulse deposition in 15 minutes timeframe. This study suggests replacement of 316 stainless steel with an aluminum oxide coating system could yield \$20M saving in capital costs for a reasonably sized system.

available reports/technical papers/presentations

John Watkins, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," Project kickoff meeting presentation, Pittsburgh, PA, January 2019. *http://www.netl.doe.gov/projects/plp-download.aspx?id=10596&filename=Inexpensive+and+Sustainable+Anti-Corrosion+Coating+for+Power+Generation+Applications.pdf*.

John Watkins, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," presented at the 2019 BP1 to BP2 Continuation Meeting Presentation, Pittsburgh, PA, August 2019. *http://www.netl.doe.gov/projects/plp-download.aspx?id=10598&filename=Inexpensive+and+Sustainable+Anti-Corrosion+Coating+for+Power+Generation+Applications.pdf*.

John Watkins, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, September 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Watkins-LTI-Anticorrosion-Coating.pdf.*

John Watkins, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Watkins.pdf.*

John Watkins, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," Final Project Briefing, Pittsburgh, PA, March 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=10601&filename=Inexpensive+and+Sustainable+Anti-Corrosion+Coating+for+Power+Generation+Applications.pdf*.

Intensified, Flexible, and Modular Carbon Capture Demonstration with Additively Manufactured Multi-Functional Device

primary project goal

Oak Ridge National Laboratory (ORNL) is engaging in process intensification as one approach to reduce carbon dioxide (CO_2) capture cost in scaled-up processes. ORNL's advanced manufacturing and chemical engineering research team is continuing the development and validation of 3D-printed intensified devices (i.e., mass exchange packing with internal cooling channels) to effectively achieve mass and heat exchange functionalities in CO_2 absorption columns at the desired scale.

technical goals

- Design, construction, and demonstration of a larger-scale column (Column B) to validate enhanced CO_2 capture with the 3D-printed intensified devices.
- Demonstrate that Column B can be modularized with the intensified devices for low aqueous advanced-solvent based capture.
- Demonstrate that Column B can be easily configured to effectively capture CO_2 from different inlet gas CO_2 compositions (i.e., coal-fired power plants and natural gas-fired power plants) and during process transients (i.e., capacity ramping up and down anticipating the intermittent nature of renewable generations).

technical content

Process intensification is considered by the U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management (FECM) Carbon Capture Program as one approach to reducing CO_2 capture cost in scaled-up processes. Process intensification with new equipment manufacturing methods has shown great potential in process footprint and construction cost reductions. Conventional solvent-based carbon capture equipment designs usually involve multiple unit operations and utilize sequentially coupled stages for mass transfer and heat transfer. In the work funded by the DOE/FECM Capture Program for FY 2018–2019 under Field Work Proposal (FWP)-FEAA130, the ORNL advanced manufacturing and chemical engineering research team has demonstrated that a 3D-printed intensified device (i.e., a mass exchange packing with built-in heat exchange channels at the device scale) can effectively achieve the mass and heat exchange functionalities at the desired scale. Testing of the 3D-printed intensified device was performed with an 8-inch diameter, 4.5-foot tall packed absorption column (Column A, Figure 1), and enhanced CO_2 capture was demonstrated for various gas and liquid flow rates for monoethanolamine (MEA).

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Post Combustion Power Generation PSC

key technology:

Enabling Technologies

project focus:

3D-Printed Intensified Devices

participant:

Oak Ridge National Laboratory (ORNL)

project number:

FWP-FEAA384

predecessor projects:

FWP-FEAA130
FWP-FEAA375

NETL project manager:

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N/A

start date:

01.01.2021

percent complete:

54%

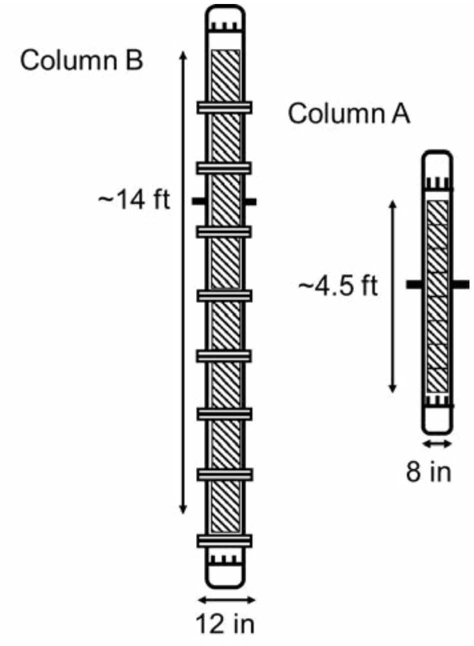


Figure 1: Eight-inch diameter, 4.5-foot tall packed absorption column (Column A) and twelve-inch diameter, 14-foot tall packed modular absorption column (Column B).

Since at-scale capture efficiency with different solvent and incoming flue gas compositions relies heavily on simultaneously approaching the thermodynamic and kinetic limits of the solvents at different locations of the absorber, a flexible and modular CO_2 capture demonstration column needs to be constructed with process intensification to further demonstrate and quantify the efficiency enhancements with one or more process-intensified devices with a scaled-up equipment design under more realistic operating conditions and under process transients.

Column B (Figure 1) is a scaled-up version of Column A. Special care is being taken during column construction to minimize heat loss through the wall and to allow for easy transfer of the intensified device from one point along the column to another. The column is constructued with modular packing units that allow movement of the intensified device to different axial positions along the absorption column height. The column is also being constructed with a liquid distributor, installed at the top of the column, based on the solvent's maximum flowrate. Special attention to safety is also key, and therefore, a heavy-duty ventilation system is being installed to dilute CO_2 in case there is a leak. In addition, the research team is developing the means to draw fluid samples along the column for chemical analysis. The objective is not only to be able to prove capture enhancement, but also to obtain experimental data that may be used for model development and validation.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	61	—
Normal Boiling Point	°C	170	—
Normal Freezing Point	°C	10.5	—
Vapor Pressure @ 15°C	bar	5.0e-04	—
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.30	—
Specific Gravity (15°C/15°C)	-	1.013	—
Specific Heat Capacity @ STP	kJ/kg-K	3.7	—
Viscosity @ STP	cP	2.5	—
Absorption			
Pressure	bar	atm.	—
Temperature	°C	40	—
Equilibrium CO_2 Loading	mol/mol	—	—
Heat of Absorption	kJ/mol CO_2	-80	—
Solution Viscosity	cP	2.0	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	120	—
Equilibrium CO_2 Loading	mol/mol	—	—
Heat of Desorption	kJ/mol CO_2	-120	—
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Integrated regeneration of solvent reduces solvent inventory.
- Modular column design provides flexibility in testing packing configurations with commercial packing and the intensified device.

R&D challenges

- Temperature control using the intensified device may be difficult for aqueous MEA, especially for natural gas flue gas.
- Controlling process transients that may push the column operation into flooding conditions.

status

ORNL has finalized a design and is in the construction phase of the project as of Q1 2022. Design and procurement of the new absorption column and its equipment were completed in 2021. Based on design comparisons with Column A, it is expected that the scale-up factor from Column A to Column B will be approximately 10-fold in terms of flue gas-throughput of the absorption column. The new modular absorption column will include approximately 14-feet of packed height and nine different packing sections. The current column configuration will use eight commercial structured packing sections and one section for the intensified device. Future experimental work may also incorporate a second intensified device for studying process intensification in multiple sections of the column. The feed gas for the absorption column will utilize a flue gas stream from a natural gas generator set operating up to 0.1 MWe base load. Solvent regeneration will be performed with a new off-line stripping column.

available reports/technical papers/presentations

Tsouris, C. and Thompson, J., "Intensified, Flexible, and Modular Carbon Capture Demonstration with Additively Manufactured Multi-Functional Device." NETL Carbon Management and Oil and Gas Research Project Review Meeting. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Tsouris.pdf*

Thompson, J. A.; Tsouris, C., Rate-Based Absorption Modeling for Postcombustion CO2 Capture with Additively Manufactured Structured Packing. *Industrial & Engineering Chemistry Research* **2021,** *60* (41), 14845-14855, doi: 10.1021/acs.iecr.1c02756.

Bolton, S., Kasturi, A., Palko, S., Lai, C., Love, L., Parks, J., Sun, X., and Tsouris, C., "3D Printed Structures for Optimized Carbon Capture Technology in Packed Bed Columns," Separation Science and Technology, 54, 2047-2058 (2019).

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/X-Sun-ORNL-Additively-Manufactured-Device.pdf*.

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/X-Sun-ORNL-Additive-Manufacturing-Utilization.pdf*.

Pilot Testing of a Highly Effective Pre-Combustion Sorbent-Based Carbon Capture System

primary project goal

TDA Research Inc. is continuing development of a new sorbent-based pre-combustion carbon capture technology for integrated gasification combined cycle (IGCC) power plants. The process uses an advanced physical adsorbent that selectively removes carbon dioxide (CO_2) from coal-derived synthesis gas (syngas) above the dew point of the gas. The project aims to prove the viability of the new technology by using data collected from the pilot plant tests to complete high-fidelity engineering and cost analyses to calculate the impact of the carbon capture system on the cost of electricity generation at a coal fired IGCC power plant and the potential of the technology to meet the U.S. Department of Energy (DOE) goals of 90% CO_2 capture and 95% purity at a cost of less than $40/tonne CO_2 captured.

Having shown promise under a previously funded DOE project (FE0000469), this sorbent is being evaluated at a larger scale, for longer durations, and under conditions that are more representative of a coal gasification-based application. Current research objectives are to collect performance data for this advanced sorbent, including two 0.1-megawatt-electric (MWe) tests with a fully equipped prototype unit using actual syngas to prove the viability of the new technology; long-term sorbent life evaluation in a bench-scale setup; the fabrication of a pilot-scale testing unit that will contain eight sorbent reactors; and the design of a CO_2 purification subsystem.

technical goals

- Enable pre-combustion CO_2 capture from syngas at 200–250°C and pressures up to 60 bar, with greater than 90% recovery and CO_2 purity of at least 95%, using a functionalized carbon sorbent in a pressure swing adsorption (PSA)-based cycle.
- Improve adsorber reactor design, including the optimized reactor internals and bed geometry through computational fluid dynamics (CFD) analysis and PSA cycle optimization with adsorption modeling.
- Complete pilot-scale field tests on syngas slipstreams at 0.1 MWe equivalent, at design conditions and for extended durations (e.g., greater than 3,000 hours), to demonstrate capability to meet all performance objectives (e.g., CO_2 removal efficiency, hydrogen [H_2] recovery, sorbent life, and performance).
- Validate long-term performance and lifetime of the sorbent through 60,000 cycles with no more than 2% decrease in adsorption capacity over fresh sorbent (enabling projected lifetime of five years for the sorbent).
- Enable improved IGCC plant efficiency (3 to 4 percentage points) over IGCC plants using conventional CO_2 removal technology, thereby improving cost of electricity in coal-based power production.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Pre-Combustion Power Generation PSC

key technology:

Sorbents

project focus:

High-Capacity Regenerable Sorbent for Coal IGCC Plants

participant:

TDA Research Inc.

project number:

FE0013105

predecessor projects:

FE0000469

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gökhan Alptekin
TDA Research Inc.
galptekin@tda.com

partners:

Gas Technology Institute; CDM Smith Inc.; University of California at Irvine (UCI); University of Alberta; Sinopec

start date:

10.01.2013

percent complete:

92%

technical content

TDA Research Inc. is designing, constructing, and operating a slipstream 0.1-MWe pilot-scale process for pre-combustion CO_2 capture to assess their novel adsorbent for the selective removal of CO_2 from syngas. The adsorbent consists of a mesoporous carbon grafted with surface functional groups that remove CO_2 via an acid-base interaction. The novel process is based on TDA's high-temperature PSA technology, using the new adsorbent to selectively remove CO_2 from syngas in an IGCC power plant. The integration of the CO_2 separation unit into the IGCC plant is shown in Figure 1.

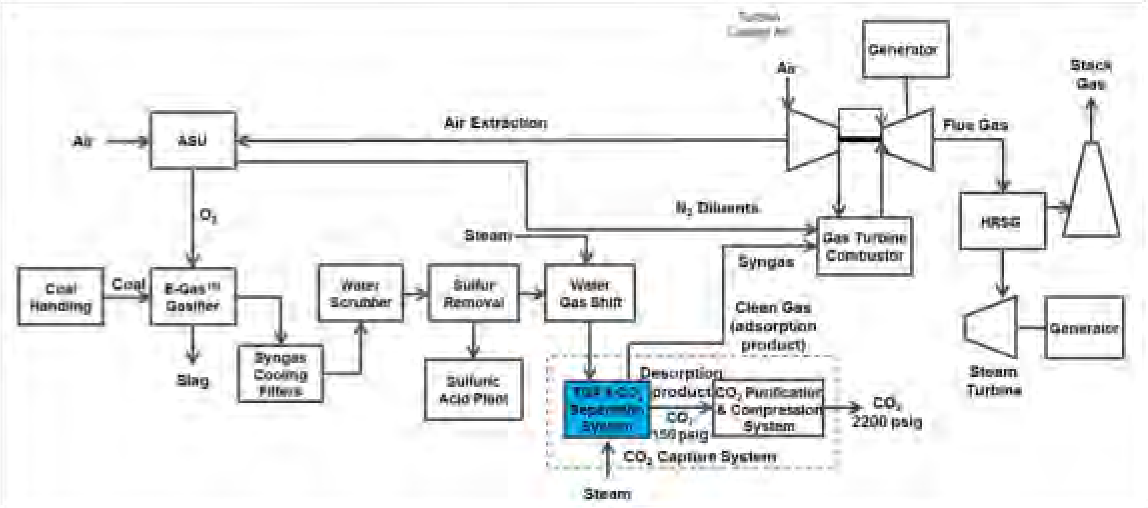


Figure 1: TDA's CO_2 capture system integration in an IGCC power plant.

The CO_2 capture system uses multiple sorbent beds that switch operating modes between adsorption and regeneration. In adsorption mode, which is operated isothermally (temperature of about 240–250°C) and at syngas pressure of about 500 pounds per square inch absolute (psia), the sorbent removes CO_2 via strong physical adsorption. The CO_2 surface interaction is strong enough to allow operation at these elevated temperatures. A detailed breakdown of the carbon capture and storage (CCS) system's operating parameters is given in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10
Temperature	°C	195.5	195.5

Equilibrium CO_2 Loading	g mol CO_2/kg	0.005	0.005	
	g mol CO_2/m^3	3.22	3.22	
Heat of Desorption	kJ/mol CO_2	28.5	28.5	
Proposed Module Design		*(for equipment developers)*		
Flow Arrangement/Operation	—	radial-flow fixed bed/cyclic		
Syngas Flowrate	kg/hr	668,083		
CO_2 Recovery, Purity, and Pressure[+]	%/%/bar	90.0%	96.0%	10
Adsorber Pressure Drop	bar	1.41		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	212.8		

[+] CO_2 is recovered at 10 bar from TDA's CO_2 capture system, which is further purified and compressed to 152.7 bar with a final CO_2 purity of 99.96%.

In regeneration mode, also operated isothermally (temperature of about 240–250°C), CO_2 is recovered via combined pressure and concentration swing by contacting the sorbent with a steam purge stream. The operating pressure ranges from 150–158 psia and partial pressure of CO_2 ranges from 0–75 psi. Because the CO_2 is recovered at approximately 150 psia, energy requirement for CO_2 compression for storage is reduced. Also, the isothermal operation eliminates heat/cool transitions, and rapid cycling reduces cycle times and increases sorbent utilization. Because the CO_2 is not bonded via a covalent bond, the energy input to the regeneration is low—only 4.9 kcal/mole of CO_2 removed (comparable to Selexol™). This energy requirement is much lower than that of the chemical absorbents (e.g., sodium carbonate [Na_2CO_3] requires 29.9 kcal/mol) and amine solvents (≈14 kcal/mol). The energy output loss of the IGCC plant is expected to be like that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO_2 capture.

The pilot plant design includes a gas conditioning unit and a high-temperature PSA-based CO_2 separation unit, as shown in Figure 2. The gas conditioning unit allows for adjustment of the concentration and purity of the syngas. The CO_2 separation unit consists of eight high-temperature sorbent beds. The design of the CO_2 capture skid for the 0.1-MW pilot unit is shown in Figure 3.

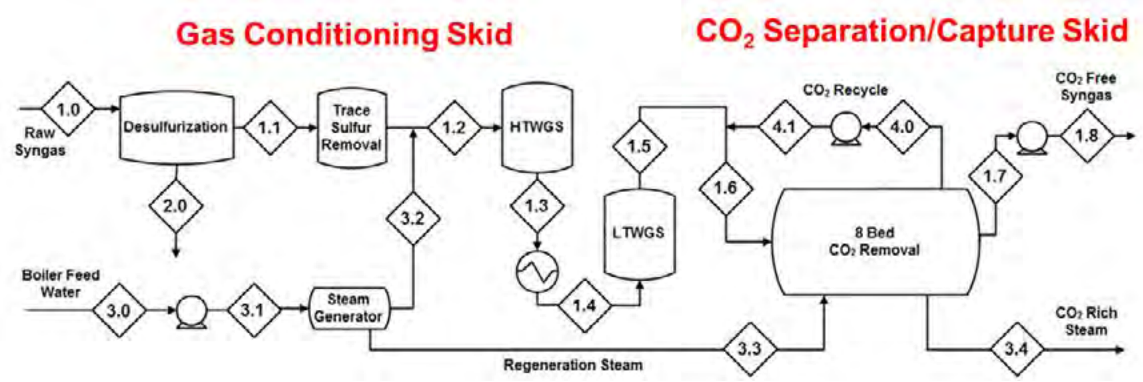


Figure 2: Flow diagram for TDA's pilot test unit.

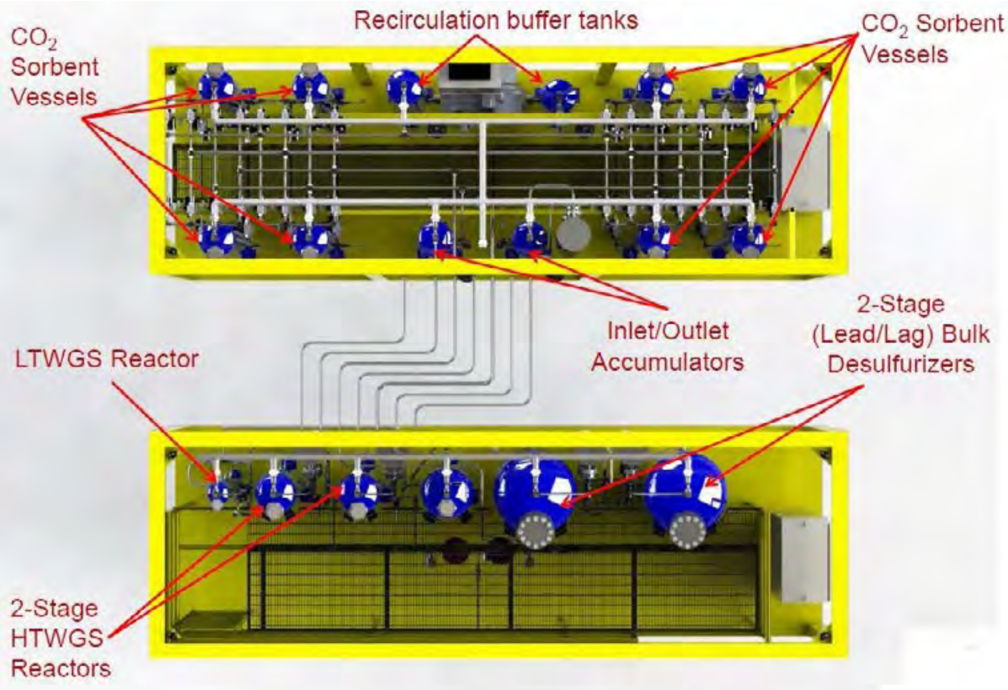
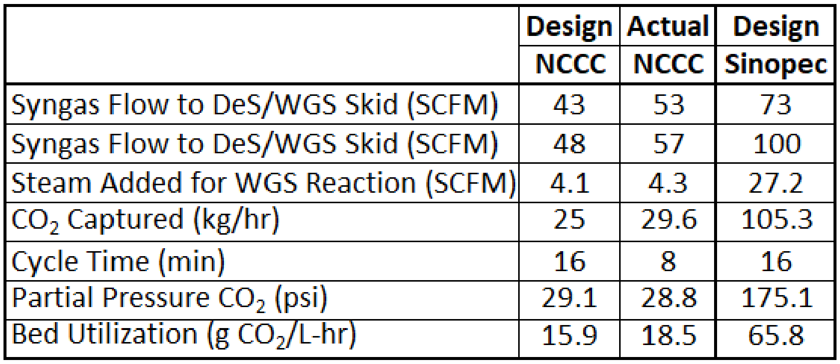


Figure 3: Overhead view of carbon capture skid.

In 2017, TDA's 0.1-MWe pilot-scale eight-bed PSA unit was installed at the National Carbon Capture Center (NCCC; Figure 4) and tested in real coal-derived syngas. The pilot unit ran for 707 hours of continuous operation at up to 97.3% carbon capture at 53 standard cubic feet per minute (SCFM) of syngas flow, exceeding design specifications. The summary results are given in Table 2. This table also shows the upcoming design performance parameters for the Sinopec oxygen-based gasifier testing at considerably increased throughput.

Figure 4: TDA's 0.1-MWe pilot unit installed in the test pad at the NCCC (Wilsonville, Alabama).

TABLE 2: SUMMARY PERFORMANCE RESULTS OF PILOT-SCALE TESTING



	Design NCCC	Actual NCCC	Design Sinopec
Syngas Flow to DeS/WGS Skid (SCFM)	43	53	73
Syngas Flow to DeS/WGS Skid (SCFM)	48	57	100
Steam Added for WGS Reaction (SCFM)	4.1	4.3	27.2
CO_2 Captured (kg/hr)	25	29.6	105.3
Cycle Time (min)	16	8	16
Partial Pressure CO_2 (psi)	29.1	28.8	175.1
Bed Utilization (g CO_2/L-hr)	15.9	18.5	65.8

In 2018 and 2019, TDA shipped, installed, and performed shakedown testing on field units at Sinopec (see Figure 5), which allow oxygen-based gasifier testing at considerably increased throughput.

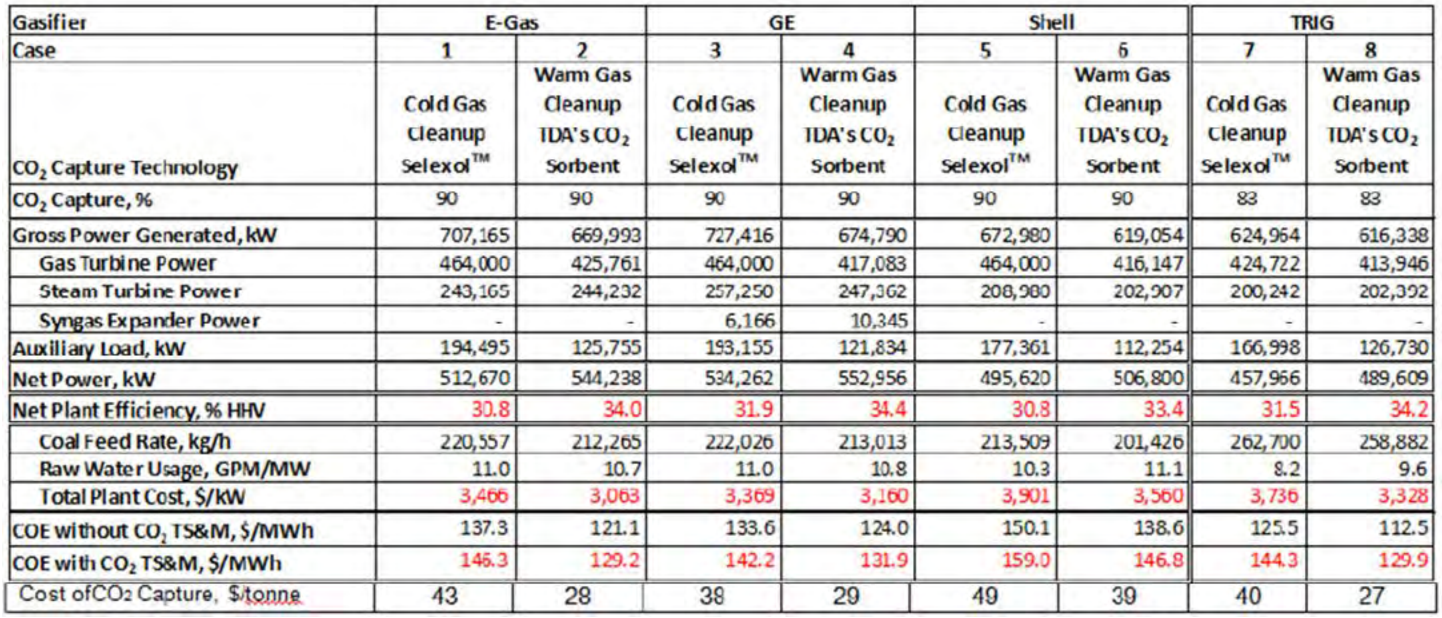
Very early testing results at 88 SCFM syngas flow have resulted in approximately 85% CO_2 removal efficiency at a rate of approximately 110 kg/hr CO_2.

TDA has also performed preliminary techno-economic analyses (TEAs) of cases assuming application of TDA's sorbent-based CO_2 capture system in IGCC plant cycles, based upon performance data available to date from recent testing. The comparisons involve a baseline of conventional cold-gas cleanup and Selexol acid gas removal, compared to TDA's assumption of warm-gas cleanup combined with the sorbent units for CO_2 capture. Results are summarized in Table 3. Overall, the findings are as follows:

- TDA system achieves higher efficiencies (34.5% and 34.1%) than IGCC with Selexol (32.0% and 31.0%) for E-Gas™ and GE gasifier-based plants.
- Cost of CO_2 capture is calculated as $31 and $30/tonne for GE and E-Gas gasifier-based plants, respectively (16–30% reduction against Selexol).
- Cost of CO_2 capture is calculated as $40 and $28/tonne for Shell and TRIG gasifier-based plants, respectively (15–28% reduction against Selexol).

Figure 5: Field test units at Sinopec, China.

TABLE 3: PRELIMINARY TECHNO-ECONOMIC COMPARISONS



Gasifier	E-Gas		GE		Shell		TRIG	
Case	1	2	3	4	5	6	7	8
CO_2 Capture Technology	Cold Gas Cleanup Selexol™	Wam Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Wam Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Wam Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Wam Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90	90	90	90	90	83	83
Gross Power Generated, kW	707,165	669,993	727,416	674,790	672,980	619,054	624,964	616,338
Gas Turbine Power	464,000	425,761	464,000	417,083	464,000	416,147	424,722	413,946
Steam Turbine Power	243,165	244,232	257,250	247,362	208,980	202,907	200,242	202,392
Syngas Expander Power	-	-	6,166	10,345	-	-	-	-
Auxiliary Load, kW	194,495	125,755	193,155	121,834	177,361	112,254	166,998	126,730
Net Power, kW	512,670	544,238	534,262	552,956	495,620	506,800	457,966	489,609
Net Plant Efficiency, % HHV	30.8	34.0	31.9	34.4	30.8	33.4	31.5	34.2
Coal Feed Rate, kg/h	220,557	212,265	222,026	213,013	213,509	201,426	262,700	258,882
Raw Water Usage, GPM/MW	11.0	10.7	11.0	10.8	10.3	11.1	8.2	9.6
Total Plant Cost, $/kW	3,466	3,063	3,369	3,160	3,901	3,560	3,736	3,328
COE without CO_2 TS&M, $/MWh	137.3	121.1	133.6	124.0	150.1	138.6	125.5	112.5
COE with CO_2 TS&M, $/MWh	146.3	129.2	142.2	131.9	159.0	146.8	144.3	129.9
Cost ofCO_2 Capture, $/tonne	43	28	38	29	49	39	40	27

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of the 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

Syngas Pretreatment Requirements – Syngas needs to be shifted to convert carbon monoxide (CO) present into CO_2 and H_2 via water-gas shift (WGS) reaction and sulfur content needs to be reduced to less than 100 parts per million (ppm) before CO_2 removal.

Sorbent Makeup Requirements – The expected life of the sorbent is five years. The annualized sorbent makeup requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 1.

Proposed Module Integration – TDA's CO_2 separation, purification, and compression systems are located downstream of the warm-gas sulfur removal and the WGS processes as shown in Figure 1.

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
497.5	388.4	30.28	0.73	2.04	0.45	39.11	26.59	<10

technology advantages

- Warm-gas CO_2 capture above dew point of syngas leads to more steam in the hydrogen-rich gas entering the turbine.
  - o Improved efficiency.
  - o Higher mass throughput to gas turbine.
  - o Lower-gas turbine temperature, which lowers the need for high-pressure nitrogen (N_2) dilution and lowers nitrogen oxide (NO_X) formation.
- High steam content feed more suited for next-generation hydrogen turbines under development.
- High working capacity and cycle life of sorbent.
- Carbon dioxide recovered at pressure reduces compression costs for storage.
- A weak CO_2 surface interaction allows fast regenerations at lower temperature with minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight, corresponding to reduced adsorber vessel size and costs.

R&D challenges

- Assuring consistency in sorbent material and minimizing batch-to-batch variation for large-scale manufacture.
- Reducing the use of purge gas during regeneration.
- Confirming resistance to syngas contaminants.

status

Pilot-scale testing at Sinopec was completed in 2020 (testing duration was shortened due to COVID-19 issues). The full TEA has been completed. Further testing is planned to continue in TDA's facilities in Colorado. Decommissioning at Sinopec is underway, and key components are being returned to TDA.

available reports/technical papers/presentations

Altepkin, G.; Jayaraman, A.; Cates, M.; Bruinsma, D.; Kugler, F.; Dippo, J., 2021, "Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System." TDA Research. Presented at the 2021 Carbon Management and Oil and Gas Research Project Review Meeting. August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_sor.pdf*.

Altepkin, G., 2021, "Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System*."* Quarterly Report #32. Submitted October 30, 2021.

"Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System," presented by Gökhan Alptekin of TDA Research, Inc. at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting – Capture and Utilization Sessions, Pittsburgh, Pennsylvania, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Precombustion-Sorbent.pdf*

"PSA Based CO_2 Capture Above the Dew Point of Synthesis Gas for IGCC Power Plants," presented at the 2017 AIChE Annual Meeting, Minneapolis, MN, November 2017. *https://www.aiche.org/conferences/aiche-annual-meeting/2017/proceeding/paper/628c-psa-based-co2-capture-above-dew-point-synthesis-gas-igcc-power-plants*

"Highly Efficient Warm Gas Carbon Capture System for IGCC Power Plants," presented at the 2016 AIChE Annual Meeting, Minneapolis, MN, November 2016. *https://aiche.confex.com/aiche/2016/webprogram/Paper470738.html*

"Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System," presented by Gökhan Alptekin, TDA Research, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2 capture/2-Tuesday/G-Alptekin-TDA-Evaluation-of-Carbon-Capture-Process.pdf*

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"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System," presented by Gökhan Alptekin, TDA Research Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Alptekin-TDA-Pre-Combustion-Sorbent-Based-Capture.pdf*

"Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System," Project Kick-Off Meeting, January 2013. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0013105-Kickoff-Pilot-Testing-PreCombustion-CO2Capture-2014-01-16.pdf*

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Alptekin, G., Jayaraman, A., Dietz, S., and Schaefer, M., "High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture," presented at the 28th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, PA, September 2011.

A High Efficiency, Modular Pre-combustion Capture System for 21st Century Power Plant Polygeneration Process

primary project goal

The overall project goal is to develop a novel, modular pre-combustion carbon capture technology platform that integrates the water-gas-shift (WGS) reaction with a physical adsorbent to eliminate carbon dioxide (CO_2) emissions, coupled with a sulfur removal process, for a coal-based polygeneration system (i.e., co-production of power and chemicals) with increased efficiency and lower cost.

technical goals

- Achieve WGS/CO_2 sorbent bed CO_2 capacity of 4 wt.% to enable an overall carbon monoxide (CO) conversion greater than 98%.
- Develop and build a test unit for integrated WGS and CO_2 adsorption with a capacity of 10 standard cubic feet per minute (SCFM) of raw syngas from coal gasification.
- Capture CO_2 at 90+% with CO_2 purified via an integrated purification subsystem to 95+%.
- Enable desulfurization via a sulfur sorbent with stable working capacity in excess of 3 wt.% hydrogen sulfide (H_2S) and not more than 10% reduction in capacity over 200 cycles, assuming syngas with inlet sulfur in the 500–1,000 parts per million (ppm) range.
- Develop a techno-economic analysis (TEA) showing that the polygeneration system can capture CO_2 at $35/tonne or lower while meeting the above CO_2 purity and capture targets.

technical content

Syngas produced by gasification contains mostly hydrogen (H_2), CO, and CO_2. In order to affect a high degree of carbon capture, it is necessary to add steam to the syngas and react it with the CO via WGS to convert the CO to more H_2 and CO_2. Carbon dioxide is extracted from the shifted syngas, leaving mostly H_2, useful for multiple applications, including decarbonized power generation, transportation fuel, chemical synthesis (e.g., ammonia), and fuels synthesis. Conventionally, a multistage WGS process with interstage cooling is required to attain substantial syngas conversion because WGS is an equilibrium-limited, exothermic reaction. The conventional multistage WGS process scheme is depicted in Figure 1. Although such WGS units can completely shift the CO to CO_2, they incur significant capital equipment and process cost, including a significant excess steam demand to suppress carbon formation on the WGS catalyst and help drive the WGS reaction to completion.

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Integrated PSA-WGS with Coal Syngas

participant:
TDA Research, Inc.

project number:
FE0031926

predecessor projects:
N/A

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Gas Technology Institute; Susteon; Clariant; University of California Irvine

start date:
10.01.2020

percent complete:
30%

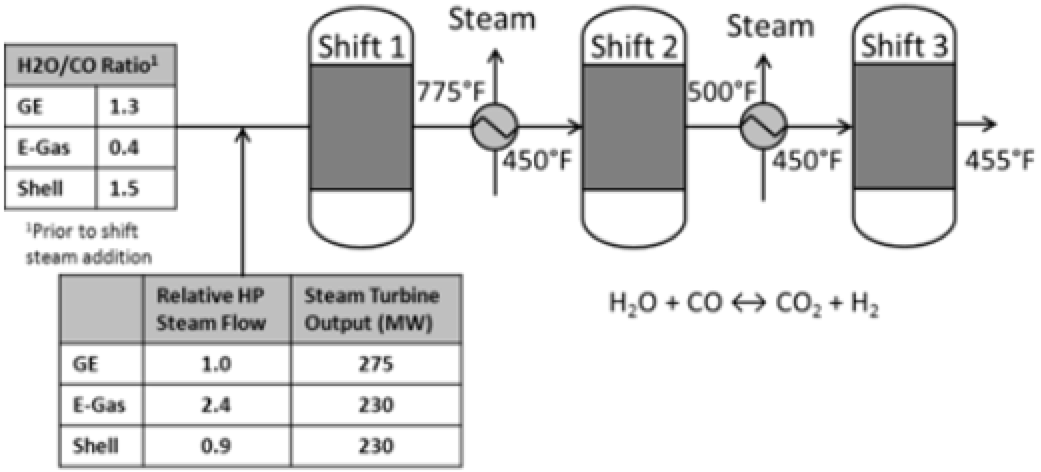


Figure 1: Three-stage, conventional WGS unit.

TDA's process approach seeks to achieve high CO conversion at low steam-to-CO ratios by combining, in the same bed, the WGS catalyst with a CO_2 sorbent capable of withstanding the temperatures experienced in a low-temperature WGS reactor as it selectively removes CO_2 from the syngas above the dew point of the gas. The proprietary sorbent consists of a mesoporous carbon grafted with surface functional groups that remove CO_2 via an acid-base interaction. The combination of the WGS and CO_2 removal improves the overall power cycle efficiency by reducing the amount of water needed for the WGS. TDA's overall process is depicted in Figure 2. Note that a high-temperature WGS reactor is followed by a single integrated low-temperature shift and CO_2 removal unit with the combined WGS catalyst and sorbent. Essentially, the conventional three-stage WGS with downstream CO_2 capture (four steps) is replaced with a two-stage WGS, with the second stage adding integrated CO_2 capture. This represents a significant degree of process intensification by reducing WGS stages and combining CO_2 capture in one of those stages.

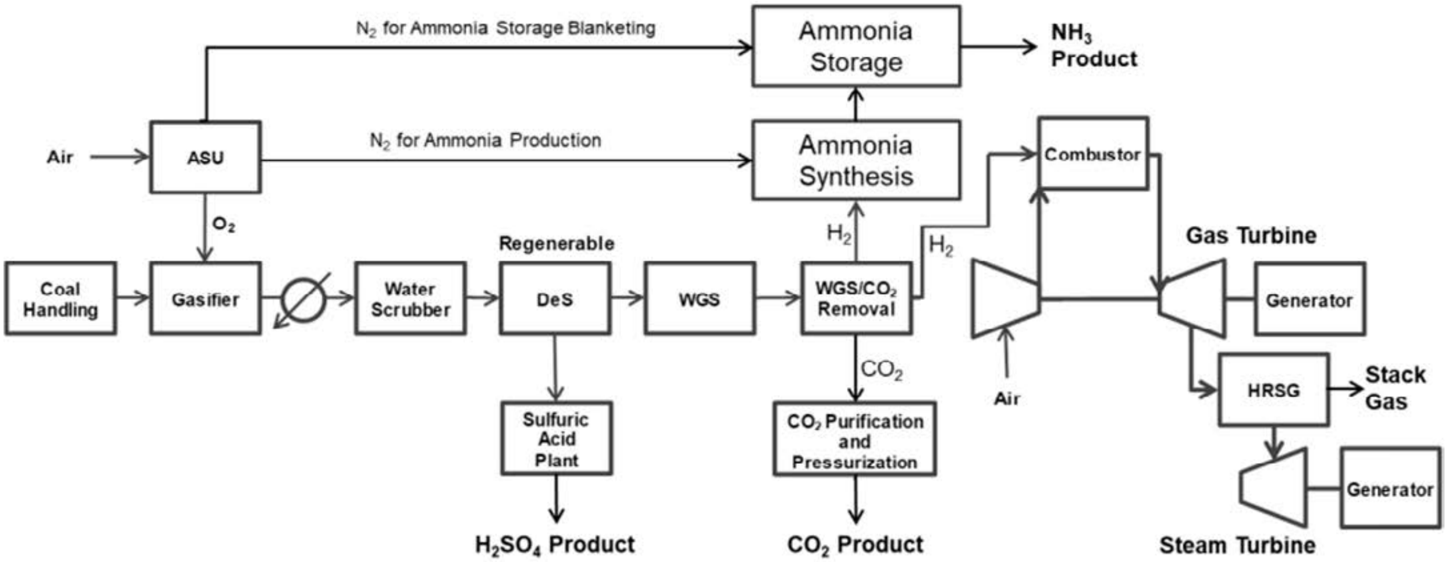


Figure 2: TDA polygeneration process concept.

The process is also integrated with a simplified fixed-bed temperature swing adsorption-based warm gas desulfurization system upstream of the WGS (using a desulfurization sorbent previously developed with the assistance of U.S. Department of Energy [DOE] funding) and contaminant removal technologies (for hydrogen cyanide [HCN] and trace metals such as silver [As], mercury [Hg], and selenium [Se]). This will ensure robust protection of the catalysts used in downstream chemical synthesis processes while maintaining the water content of the gas to achieve high efficiency in polygeneration schemes. In the present process concept, ammonia synthesis from hydrogen produced is assumed as a polygeneration pair to decarbonized power generation using the hydrogen, here consisting of a typical combined cycle with gas turbine topping and steam turbine bottoming cycle. The process also includes a catalytic CO_2 purification process essential to attain CO_2 product purity requirements (residual CO and oxygen [O_2] in the CO_2 product must be reduced to very low levels for utilization in enhanced oil recovery [EOR] application).

Figure 3 depicts the combined WGS and CO_2 adsorber reactor column that has been demonstrated at bench scale. The basic engineering deployed in the column is diagrammed.

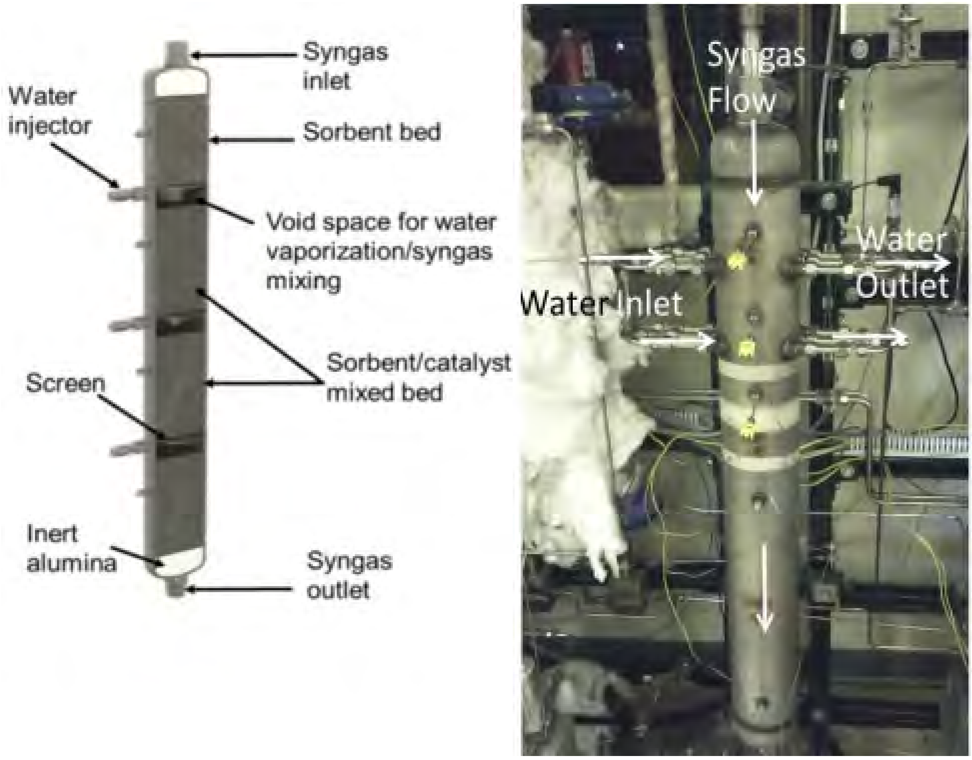
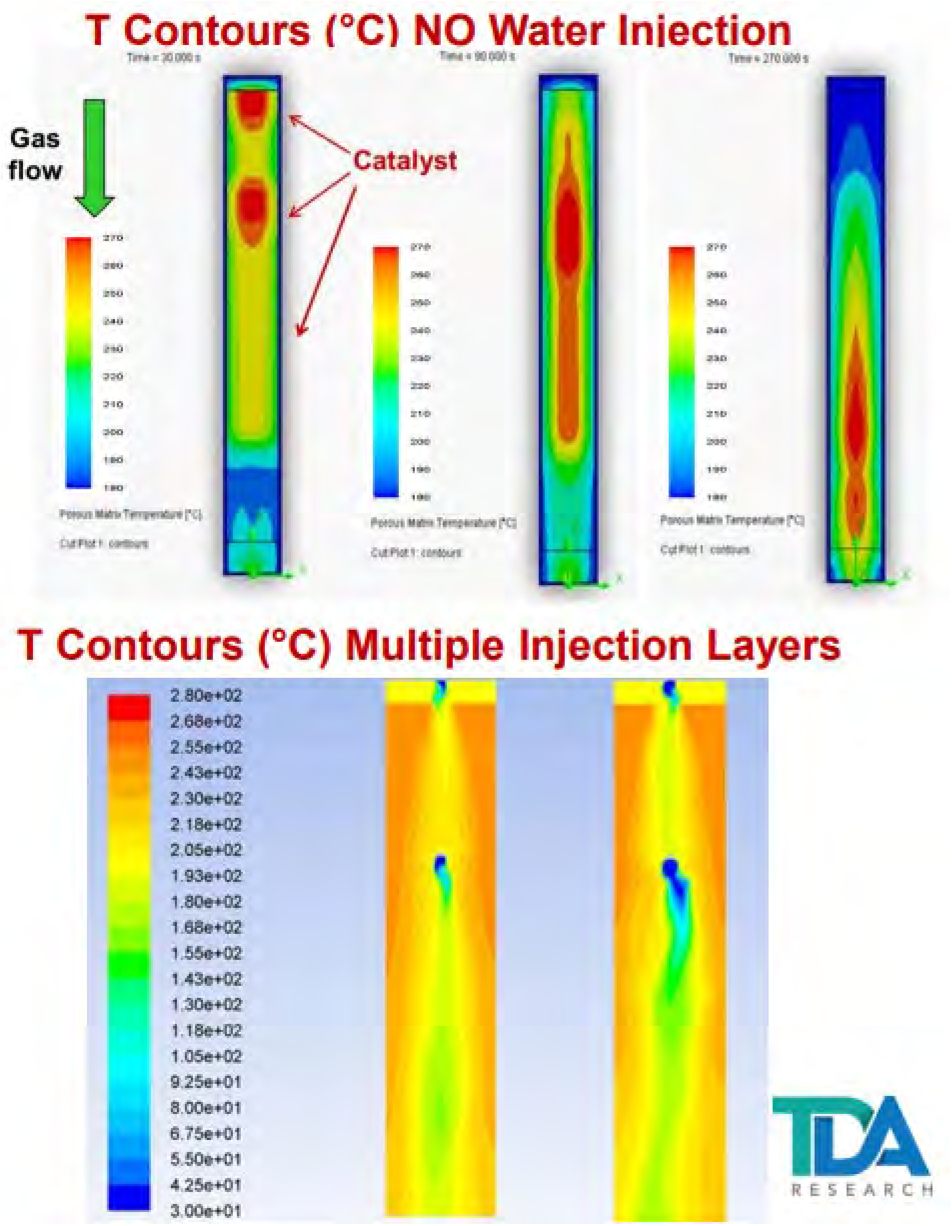


Figure 3: Bench-scale WGS and CO_2 adsorption column.

Combining WGS catalyst and CO_2 sorbent in the same column creates challenges in the form of proper heat management and temperature control. Uniform temperature without hot or cold spots is required for both optimal WGS conversion of the CO in the syngas and CO_2 removal from the syngas. TDA found that advanced heat management based on direct water injection greatly improves temperature control, and that optimal temperature rise occurs when the WGS catalyst is distributed into two layers with water injections before each layer. This is depicted in Figure 4; the top image of Figure 4 shows large, unfavorable temperature variations in a reactor column not employing water injection, while the bottom image of the figure shows excellent temperature uniformity and control attained with staged water injection and two-layer WGS catalyst distribution.


T Contours (°C) NO Water Injection

T Contours (°C) Multiple Injection Layers

Figure 4: Heat-integrated WGS and CO_2 capture.

The integrated WGS and CO_2 capture system uses multiple columns that switch operating modes between adsorption and regeneration of the CO_2 sorbent. Pressure is high for adsorption (up to 500 pounds per square inch gauge [psig]) and low for regeneration (50–65 psig), constituting the CO_2 removal as a pressure swing adsorption (PSA) cycle. The alternating modes are obviously required for operation of the CO_2 sorbent, not the WGS catalyst, which raises the question of whether the pressure cycling has any adverse effect on the WGS catalyst. TDA completed 32,000 cycles of the combined WGS catalyst and sorbent and determined that catalytic activity of the WGS catalyst was unaffected. Temperature is relatively isothermal (200–215°C), which is ideal for sorbent performance. In quantifying sorbent performance, TDA determined heat of adsorption at 5–7 kcal/mol and measured CO_2 capacities as a function of pressure, as shown in Figure 5. TDA's target for capacity was 4 wt.% CO_2 at 500 psi; this was well exceeded with 6.2 wt.% achieved at that pressure.

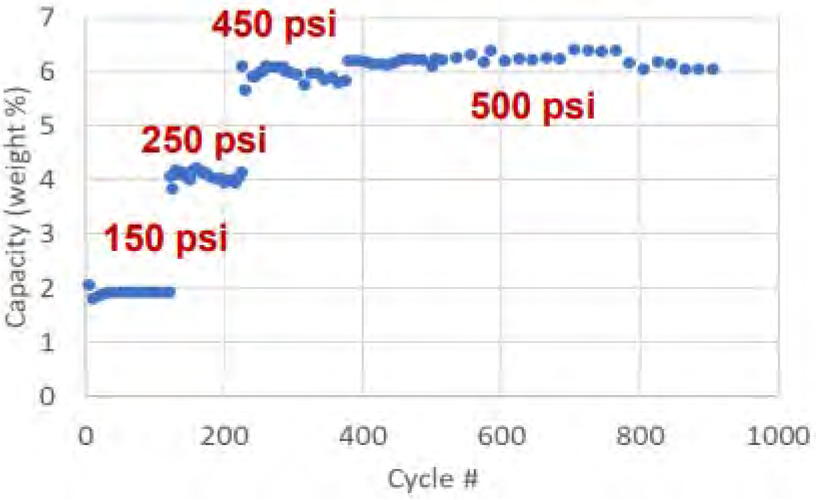


Figure 5: TDA capture sorbent CO_2 capacity.

The offgas from regeneration of the combined WGS and CO_2 sorbent columns is high in CO_2 but does contain H_2, methane (CH_4), and CO as minor constituents, which must be removed or converted to achieve pipeline quality, consistent with typical use of the product CO_2 in EOR. Accordingly, a CO_2 purification subsystem is necessary. The subsystem process is depicted in Figure 6. It uses oxygen (sourced from the main air-separation unit [ASU] associated with the gasifier) in a catalytic oxidizer, and excess oxygen downstream of the catalytic oxidation step is dealt with by leveraging trace oxygen removal sorbents previously developed for removing residual oxygen from oxy-combustion processes (refer to National Energy Technology Laboratory [NETL] project FE0029090).

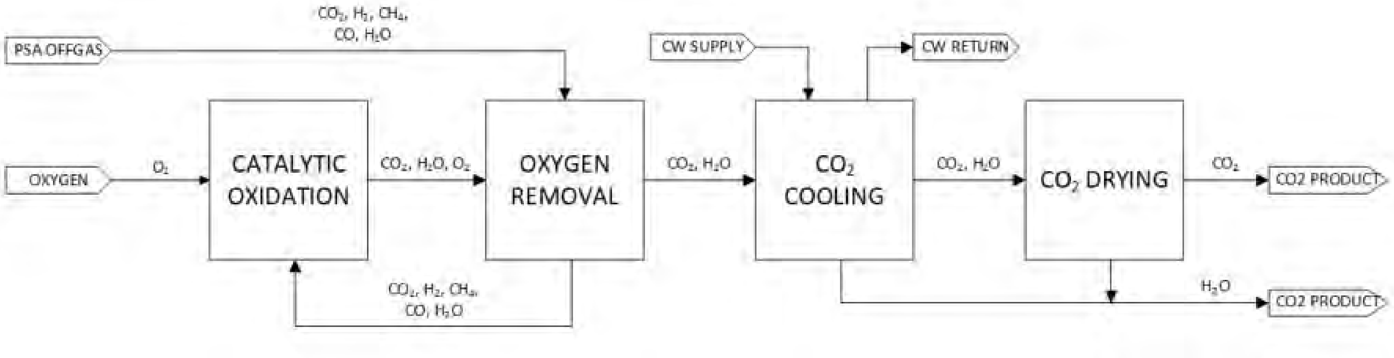


Figure 6: CO_2 purification subsystem.

TDA is currently developing a test unit designed to treat 10 SCFM of actual syngas flow. This will deploy eight sorbent beds and two accumulator tanks. The test unit will contain three sub-assemblies/skids: (1) integrated WGS and CO_2 separation skid with the new column/reactor design, (2) a regenerable warm gas desulfurization gas processing skid, and (3) a CO_2 purification skid. It is planned that testing will occur at partner GTI's pilot gasifier test site, using real syngas generated by either the fluidized bed U-GAS® gasifier or the R-GAS™ gasifier pilots that GTI has onsite.

Figure 7: Eight-column integrated WGS and CO_2 capture unit.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10
Temperature	°C	195.5	195.5
Equilibrium CO_2 Loading	g mol CO_2/kg	0.005	0.005
	g mol CO_2/m^3	3.22	3.22
Heat of Desorption	kJ/mol CO_2	28.5	28.5
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	radial-flow fixed bed/cyclic	
Syngas Flowrate	kg/hr	668,083	
CO_2 Recovery, Purity, and Pressure[+]	%/%/bar	90.0% 96.0% 10	
Adsorber Pressure Drop	bar	1.41	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	212.8	

[+] CO_2 is recovered at 10 bar from TDA's CO_2 capture system, which is further purified and compressed to 152.7 bar with a final CO_2 purity of 99.96%.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as H_2S, carbonyl sulfide (COS), ammonia (NH_3) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

Syngas Pretreatment Requirements – Syngas sulfur content needs to be reduced to less than 100 parts per million (ppm) before WGS and CO_2 removal.

Sorbent Make-Up Requirements – The expected life of the sorbent is five years. The annualized sorbent make-up requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 2.

Proposed Module Integration – TDA's combined WGS and CO_2 removal module is located downstream of the syngas desulfurization unit as shown in Figure 2; syngas composition and conditions entering module are as follows:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
722.2	388.4	28.30	8.16	0.10	0.54	44.76	17.46	<10

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	28.1	35.0
Cost of Carbon Avoided	\$/tonne CO_2	69.9	70.0
Capital Expenditures	\$/tonne CO_2	13.7	15.0
Operating Expenditures	\$/tonne CO_2	14.4	20.0

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The TEA numbers provided in the Table for both current and target values are all based on Rev. 2a DOE Baseline Study. Capital expenditures are \$ per tonne CO_2 captured, based on the recommended capacity charge factor of 0.124 in Rev. 2a DOE Baseline Study.

Scale of Validation of Technology Used in TEA – The numbers were from modeling data that was validated from pilot-scale testing.

technology advantages

- Warm gas removal of CO_2, sulfur, and contaminants improves process efficiency.
- Reducing the use of excess steam improves power cycle efficiency by lowering parasitic energy requirements for the process.
- Process intensification should reduce the number of hardware components and their cost.

R&D challenges

- Integrated WGS and CO_2 adsorption results in higher temperatures as heat from the exothermic WGS reaction accumulates in the beds—this makes CO_2 capture more difficult.
- Achieving more uniform cooling of the WGS and CO_2 adsorption bed without having hot or cold spots.
- Need for modular warm gas sulfur removal technologies.

status

TDA finished detailed design of the integrated WGS and CO_2 removal skid, CO_2 purification skid, and regenerable sulfur skid, and performed various tests of the CO_2 purification catalyst and regenerable sulfur sorbent. The preliminary TEA shows favorable polygeneration plant efficiencies for combined electricity and ammonia production.

available reports/technical papers/presentations

"A High Efficiency, Modular Pre-combustion Capture System for CoalFIRST Poly-generation Process," Project Kickoff Presentation, November 3, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11001&filename=A+High+Efficiency%2c+Modular+Pre-combustion+Capture+System+for+CoalFIRST+Poly-generation+Process.pdf*

"A High Efficiency, Modular Pre-Combustion Capture System for CoalFIRST Poly-generation Process," presented by Gokhan Alptekin and Ambalavanan Jayaraman, TDA Research Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Alptekin_cap.pdf*

Critical Component/Technology Gap in 21st Century Power Plant Gasification-Based Polygeneration: Advanced Ceramic Membranes/Modules for Ultra-Efficient H_2 Production/CO_2 Capture for Coal-Based Polygeneration Plants

primary project goal

Media and Process Technology Inc. (MPT), in collaboration with the University of Southern California, is advancing inorganic membrane technology for pre-combustion carbon dioxide (CO_2) capture from syngas in a gasification-based polygeneration plant. The primary project goal is two-fold: (1) to transition the current single-ended “candle filter” configuration of the ceramic membrane support to a dual-end (open both ends), full ceramic multiple-tube bundle configuration that will enable permeate sweep/purge capability; and (2) to develop the housing design for the dual-end bundles with emphasis on minimization of stresses associated with the membrane to housing seals and incorporation of multiple bundles into a pre-commercial-scale unit.

technical goals

- Demonstrate durability/robustness of the full ceramic multiple-tube membrane bundle and multi-bundle module at operating conditions of up to 400°C and at up to 800 pounds per square inch gauge (psig). Testing syngas flowrate is to be 10 standard cubic feet per minute (SCFM).
- Achieve the greater than 30% cost of electricity (COE) cost savings target for CO_2 capture relative to baseline capture costs.
- Develop, fabricate, and demonstrate a membrane module incorporating multiple membrane bundles in a series-parallel configuration with permeate purge capability.
- Conduct long term performance stability testing of multiple membrane bundles in the dual-end configuration.

technical content

Gasification-based polygeneration takes advantage of the primary gasification product, hydrogen (H_2), not only as fuel for power generation, but also a feedstock for chemicals production (specifically ammonia [NH_3] in this case) in conjunction with co-produced nitrogen (N_2). Polygeneration confers the ability to rapidly adjust

program area:
Point Source Carbon Capture

ending scale:
Small Pilot

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Ceramic Membranes with Coal Syngas

participant:
Media and Process Technology Inc.

project number:
FE0031930

predecessor projects:
N/A

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partners:
University of Southern California

start date:
10.01.2020

percent complete:
40%

the plant output to market need, and enhances suitability of gasification-based processes in smaller-scale, distributed co-production facilities. Carbon capture from syngas is essential to yield H_2 for NH_3 synthesis or for decarbonized power generation in these cycles.

Conventionally, carbon capture is based on amine solvent-based capture (e.g., Selexol) requiring cooling of the syngas to low temperatures. However, plant efficiency can be greatly improved by H_2-CO_2 separations from warm syngas using alternative technology. MPT has developed an inorganic/ceramic membrane-based Dual-Stage Membrane Process (DSMP, DE-FE0013064), which eliminates the need for a high-cost conventional two-stage, Selexol-based CO_2 capture process. The membranes themselves consist of carbon molecular sieve, palladium, zeolites, or zeolitic imidazolate framework (ZIF) applied via thin active layer deposition on ceramic substrate. Membrane-based unit operation is recognized for its simplicity, modular configuration, and quick turn-up/turn-down, making it well suited for small-scale distributed production facilities. Figure 1 depicts the overall polygeneration cycle, in this case showing where the inorganic membrane-based warm/hot gas processing unit fits into the cycle for polygeneration of power and NH_3.

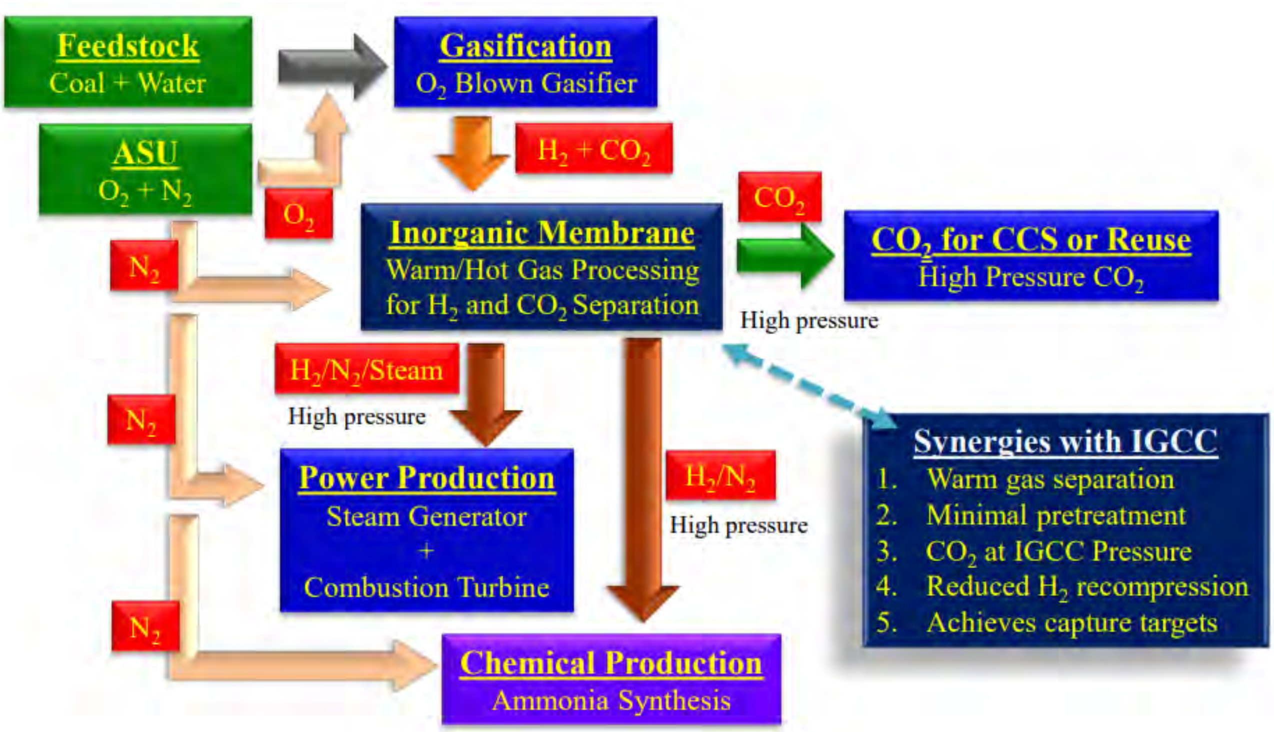

Figure 1: Inorganic membrane technology role in polygeneration cycle.

For the DSMP (and any membrane process in pre-combustion capture) to operate commercially, permeate sweep/purge with high-pressure N_2 (from the air separation unit [ASU]) and/or steam (from steam cycle of the power generating unit) is required. Unfortunately, this "permeate purge" capability is not currently available in large-format inorganic membranes rated for use at temperatures above approximately 200°C. MPT has prepared multiple-tube membrane bundles for high-temperature gas separation service (up to approximately 450°C; greater than 1,200 psig) that have been performance-demonstrated at the National Carbon Capture Center (NCCC). However, these bundles were fabricated in a "candle filter" configuration and are not permeate purgeable. Thus, the critical technology gap for the proposed process to be implemented commercially in polygeneration operation mode is the development of a purgeable inorganic membrane module. Such a module includes multiple dual-end open bundles in a series/parallel configuration, introducing additional technical challenges to be overcome such as inter-bundle sealing and shell-side feed flow distribution. Figure 2 depicts the concept for the permeate purgeable multiple bundle housing, bundles, and seals in question.

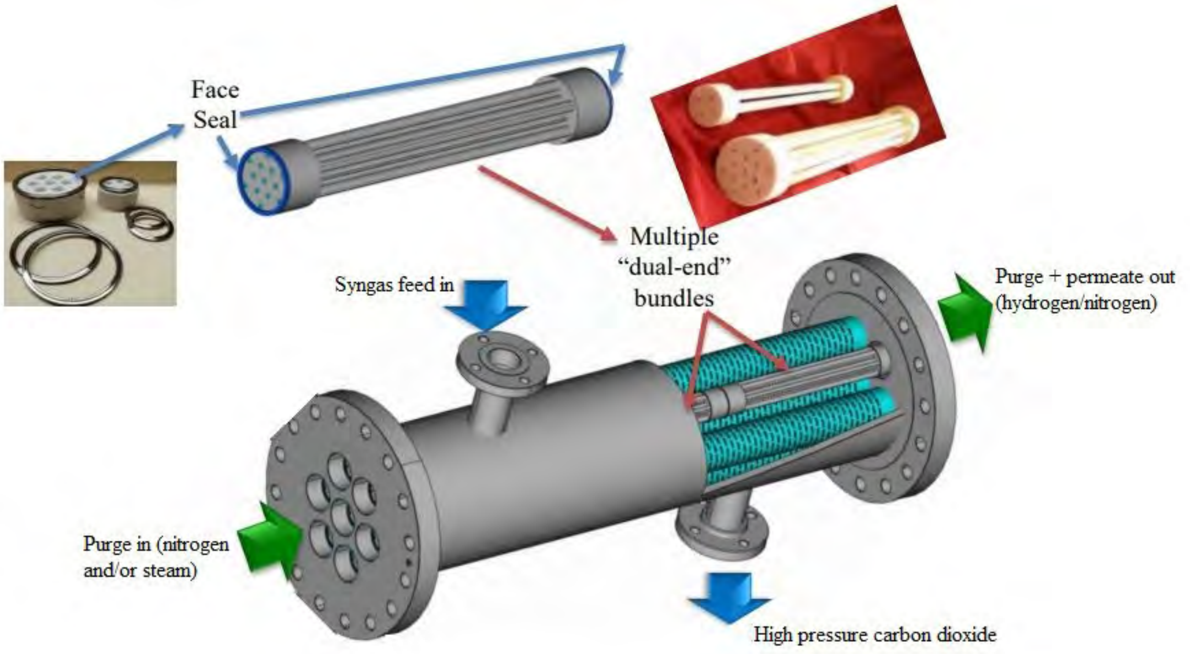

Figure 2: Permeate purgeable multiple bundle housing and seals.

Current technology development work consists of developing and fabricating a permeate purgeable multiple-tube bundle, with attention to the bundle housing with appropriate seals. Bundles sized up to 4-inch diameter and up to 38-inch length are ultimately targeted; a 1.5-, 2-, and 3-inch diameter, 38-inch dual-end bundle has been successfully fabricated.

A range of challenge tests to demonstrate bundle/housing stability are to be conducted, leading to long-term mechanical/performance stability testing (six to 12 months) at the target operating conditions. Computational fluid dynamics (CFD) modeling to simulate feed flow distribution is in process, with the idea of incorporating the CFD model into gas separation models, to use modeling to inform bundle/module configuration, and to verify mixed gas separation with model predictions. Figure 3 depicts some single-tube modeling results showing gas species concentrations.

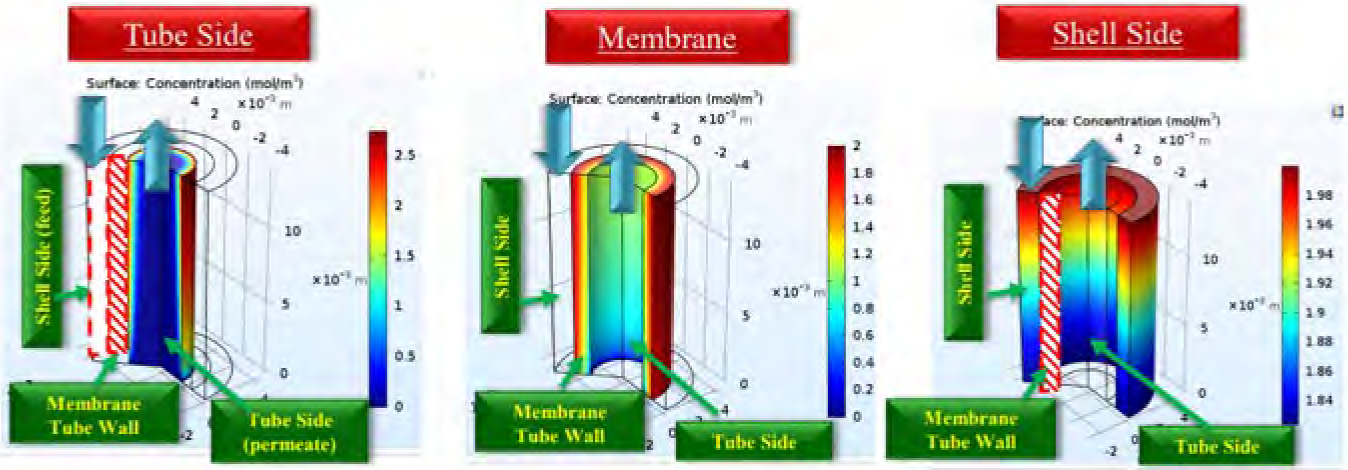

Figure 3: Single-tube membrane CFD gas concentration analysis.

Findings on performance of a commercially viable, purgeable module will inform a DSMP techno-economic analysis (TEA) for the polygeneration plant case. Both Carbon Molecular Sieve (CMS) and palladium alloy (Pd-Ag and Pd-Cu) have been previously performance-tested including multiple-tube membrane bundles at the NCCC. Membrane process parameters for these membranes (CMS Membrane #1 and Pd alloy Membrane #2) are summarized in Table 1A and 1B, respectively.

TABLE 1A: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #1)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Carbon Molecular Sieve (CMS)	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 3	2 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	hour	>1,500 in coal gasifier syngas (NCCC)	>20,000
Manufacturing Cost for Membrane Material	$\$/m^2$	2,400	<1,200
Membrane Performance (Membrane #1)			
Temperature	°C	250 to 300	250 to 300
H_2 Pressure Normalized Flux	GPU	350 to 750	350 to 750
H_2/H_2O Selectivity	—	2 to 4	2 to 4
H_2/CO_2 Selectivity	—	>50	>80
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>5,000	>5,000
Type of Measurement	—	Mixed gas and gasifier offgas (NCCC)	Same

TABLE 1B: MEMBRANE PROCESS PARAMETERS

Materials Properties (Membrane #2)	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Palladium Alloy	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Selective Layer	µm	2 to 5	1 to 3
Membrane Geometry	—	Tubular	Tubular
Maximum Trans-Membrane Pressure	bar	>80	>80
Hours Tested without Significant Degradation	—	>35,000 hours in lab testing >150 in pre-treated coal gasifier syngas (NCCC)	>2,000 hours in laboratory simulated syngas
Manufacturing Cost for Membrane Material	$\$/m^2$	9,500	<4,500
Membrane Performance (Membrane #2)			
Temperature	°C	350 to 450	350 to 450
H_2 Pressure Normalized Flux	GPU (at 20psig)	2,000 to >5,500	2,000 to >5,500
H_2/H_2O Selectivity	—	>3,000	>5,000
H_2/CO_2 Selectivity	—	>3,000	>5,000
H_2/H_2S Selectivity	—	NA (high)	NA (high)
Sulfur Tolerance	ppm	<50	<50
Type of Measurement	—	Mixed gas and pretreated gasifier offgas (NCCC)	Same
Proposed Module Design			
Flow Arrangement	—	Co-, counter-, or cross flow	
Packing Density	m^2/m^3	>450	
Shell-Side Fluid	—	Feed/retentate	

Syngas Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90	~95	>50
H_2 Recovery, Purity, and Pressure	%/%/bar	>98.8	>97	5 to 15
Pressure Drops Shell/Tube Side	bar		Unknown	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		Housing cost is estimated at ca. \$350 to \$700/m^2.	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Membrane Permeation Mechanism – CMS Membrane: Molecular Sieving; Pd Alloy Membrane: Solution-Diffusion.

Contaminant Resistance – CMS Membrane: Resistant to all coal/biomass gasifier off-gas contaminants; Pd Alloy Membrane: Sulfur species are a significant problem. Unknown for other gas phase contaminants.

Syngas Pretreatment Requirements – CMS Membrane: None except upstream particulate removal at >50µm.

Pd Alloy Membrane: Desulfurization required.

Membrane Replacement Requirements – Unknown; assume 10 years.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Design – See Figure 2. Composition of gas entering the membrane subsystem is assumed to be:

Pressure	Temperature	Composition						
		vol%						ppmv
psig	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
800	550	27	6	<1	<1	41	25	500

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE / DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	33.2	21.5
Capital Expenditures	\$/tonne CO_2	644	644
Operating Expenditures	\$/tonne CO_2	26.3	26.3

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – This work has been developed using Case B5B of DOE/NETL Report 2015/1727 – “Cost and Performance Baseline for Fossil Energy Plants,” Volume 1b Rev 2b, July 31, 2015, GEE IGCC with CO_2 Capture as the base case.

Scale of Validation of Technology Used in TEA – Testing was conducted at the NCCC with pilot scale multiple tube membrane bundles at gasifier syngas feed rates up to 5 scfm.

technology advantages

- Inorganic membranes have been demonstrated to be highly effective for and ideally suited to pre-combustion capture.
- Warm gas removal of CO_2, sulfur, and contaminants minimizes gas recompression demand and improves process efficiency.
- Potential for greater than 40% reduction in COE versus baseline amine solvent-based capture.
- DSMP modified polygeneration cycle is well suited to co-production of NH_3.

R&D challenges

- Permeate purge capability with nitrogen or steam is assumed in various technoeconomic analyses, but not yet available in practice.
- Multiple bundle housing design concerns and restrictions: minimizing stress between the ceramic membrane bundles and steel housing, and maintaining bundle interconnects that maintain axial compression.
- Multiple bundle feed flow maldistribution (shell side) resulting in poor mixed gas performance. CFD modeling is being developed for the configuration shown in Figure 2.

status

Dual-ended multiple-tube membrane bundle fabrication scale-up is in process with increasing diameters (1.5-inch and 2-inch diameter scales to 3 inches) being worked on, along with thermal cycling challenge testing. There has been a successful test of a prototype high-temperature testing rig to 400°C and 800 psig. CFD model development and testing continues.

available reports/technical papers/presentations

“Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants,” Project Budget Period 1 Review Meeting, March 11, 2022. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13015&filename=Critical+Component%2fTechnology+Gap+in+21st+Century+Power+Plant+Gasification+Based+Poly-*

generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf.

"Critical Component/Technology Gap in 21st Century Power Plant Gasification Based Poly-Generation: Advanced Ceramic Membranes/Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Presented by Richard Ciora, Media and Process Technology, Inc., 2021 NETL Carbon Management Research Project Review Meeting, August 13, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ciora.pdf.*

"Critical Component/Technology Gap in Coal FIRST Gasification Based Poly-generation: Advanced Ceramic Membranes/ Modules for Ultra Efficient H_2 Production/CO_2 Capture for Coal-Based Poly-generation Plants," Project Kickoff Meeting, November 5, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11008&filename=Critical+Component%2fTechnology+Gap+in+Coal+FIRST++Gasification+Based+Poly-generation%3a+++Advanced+Ceramic+Membranes%2fModules+for+Ultra+Efficient++H2+Production%2fCO2+Capture+for+Coal-Based+Poly-generation+Plants.pdf.*

Sorption-Enhanced Mixed Matrix Membranes for Hydrogen Purification and Carbon Dioxide Capture

primary project goal

This work focused on combining crosslinked polymers having molecular size-sieving ability, and palladium (Pd)-based nanomaterials with very high hydrogen (H_2)/carbon dioxide (CO_2) solubility selectivity, to achieve membranes with superior gas-separation performance relative to stand-alone polymeric membranes. The primary goal was to advance the new generation of membrane materials that combine robust performance with good processability to significantly decrease the cost of CO_2 capture, utilization, and storage (CCUS), enabling environmentally responsible energy production from abundant domestic coal.

technical goals

- Identify mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 at 150 to 200°C with simulated syngas.
- Prepare thin-film mixed matrix composite membranes with H_2 permeance of 500 gas permeation units (GPU) and H_2/CO_2 selectivity of 30 at 150 to 200°C and perform parametric testing of these membranes using simulated syngas in the laboratory.
- Conduct a 20-day field test of membrane stamps with real syngas from a gasifier, providing duration testing as well as assessing effects of exposure to syngas contaminants.

technical content

The State University of New York (SUNY) developed membrane technology as an energy-efficient and low-cost approach for pre-combustion CO_2 capture and H_2 purification in integrated gasification combined cycle processes. The key advancement of this technology was a series of novel sorption-enhanced mixed matrix membranes (MMMs) with high H_2 permeance (500 GPU) and high H_2/CO_2 selectivity (30) at temperatures up to 200°C. The approach combined highly crosslinked polymers with strong molecular size-sieving ability and Pd-based nanomaterials with high H_2/CO_2 selectivity to achieve membranes with performance superior to stand-alone polymeric membranes.

The working hypothesis explored in this technology development was that Pd nanoparticles exhibit extraordinary H_2 sorption, and therefore would confer favorable H_2/CO_2 solubility selectivity to thin-film composite (TFC) membranes into which they are incorporated (allowing H_2 to "hop" along the particle array). Such membranes, consisting of metallic Pd particles dispersed in a polymer matrix, are termed MMMs. Figure 1 depicts this approach, in which an MMM should improve both permeance and selectivity for H_2 separation above those typical of base polymer membranes.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Pre-combustion Power Generation PSC

key technology:

Membranes

project focus:

Mixed Matrix Membranes with Coal Syngas

participant:

State University of New York (SUNY)–Buffalo

project number:

FE0026463

predecessor projects:

N/A

NETL project manager:

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partners:

Membrane Technology and Research Inc.

start date:

10.01.2015

percent complete:

100%

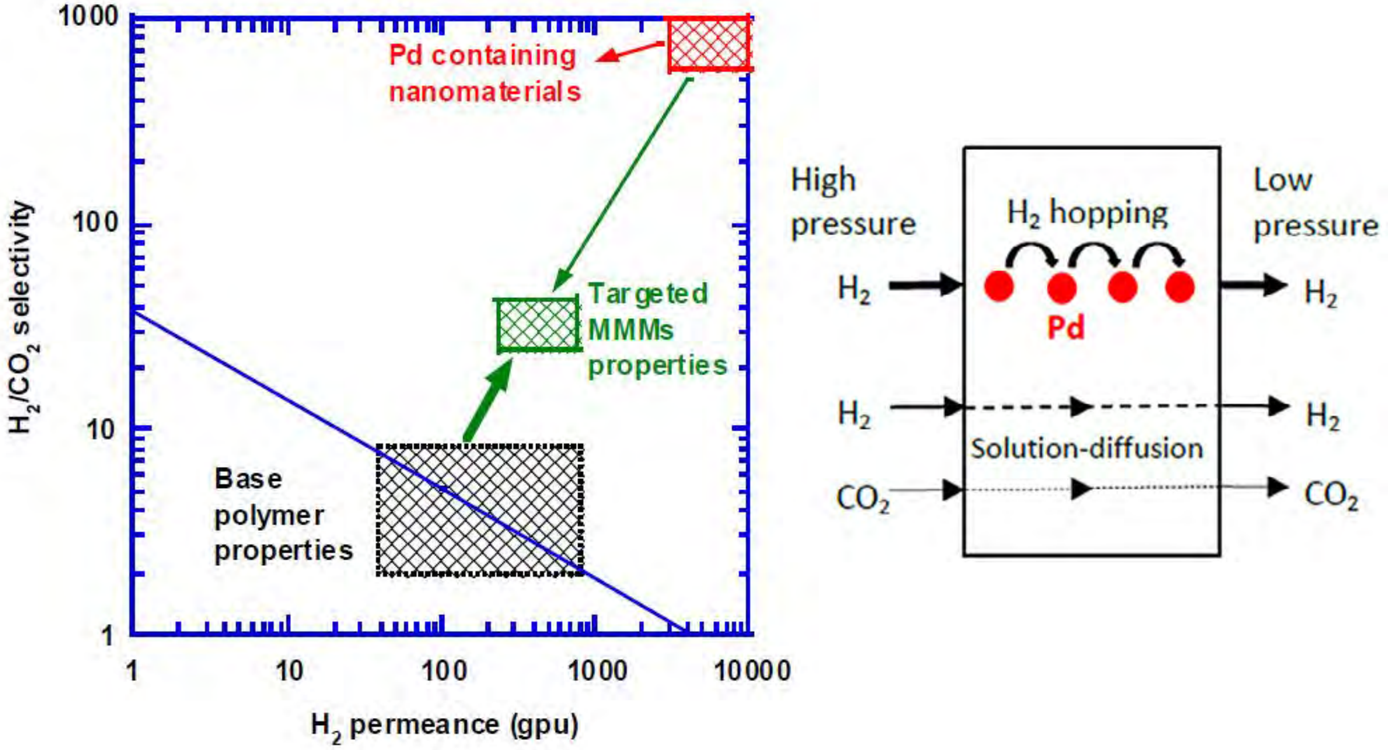

Figure 1: Mixed matrix materials approach.

One of the most suitable choices of polymeric material for membranes intended for H_2 separation from hot syngas is poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (m-PBI), a rigid polymer with strong size-sieving ability, and which has been widely investigated for elevated temperature H_2/CO_2 separation. One of the strategies to enhance the size-sieving ability in m-PBI is to crosslink the polymer chains to increase chain rigidity and/or decrease free volume, and in this work, the m-PBI was crosslinked using terephthaloyl chloride. SUNY also discovered that by doping with phosphoric acid (H_3PO_4), the PBI is favorably modified toward greater H_2/CO_2 selectivity while decreasing H_2 permeability. The H_3PO_4 tightens the polymer structure and increases size-sieving ability while exhibiting stability up to 200°C. The improvement in PBI polymer properties thus demonstrated is depicted in Figure 2.

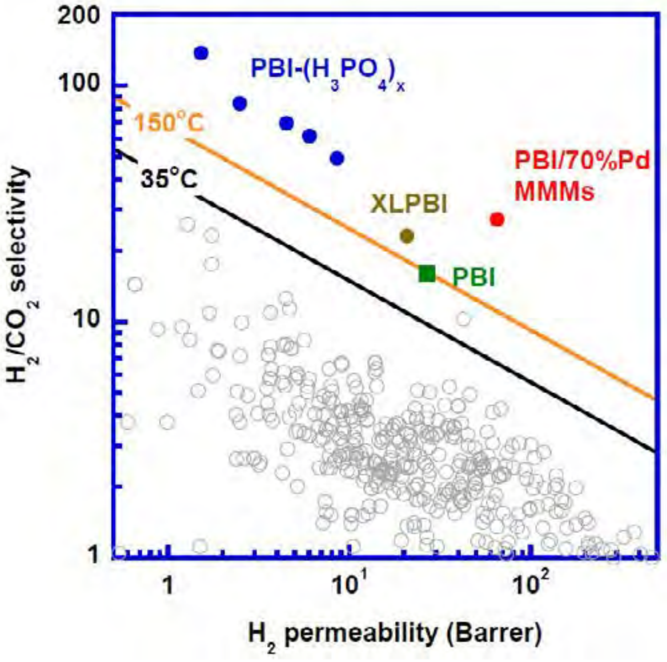

Figure 2: Polymer development and scale-up.

An important aspect of development of this technology was synthesis of the Pd nanoparticles for incorporation in the MMMs. Both solution-phase (colloidal) synthesis and gas-phase (aerosol) synthesis using a high-temperature reducing jet (HTRJ) reactor developed by SUNY were investigated. This reactor is depicted in Figure 3. The solution-phase synthesis directly provides nanoparticles that are dispersible in common organic solvents, including those from which the polymer membranes are cast. However, the HTRJ process can more readily produce alloy nanoparticles and is likely to be a more scalable and cost-effective process at larger scale. Pd-copper (Cu) (60/40) alloy nanoparticles with typical size of 4 to 8 nm were successfully prepared using the HTRJ reactor; when tested, these evidenced extremely high H_2/CO_2 solubility selectivity (≈840), and H_2 chemisorption independent of gas pressure.

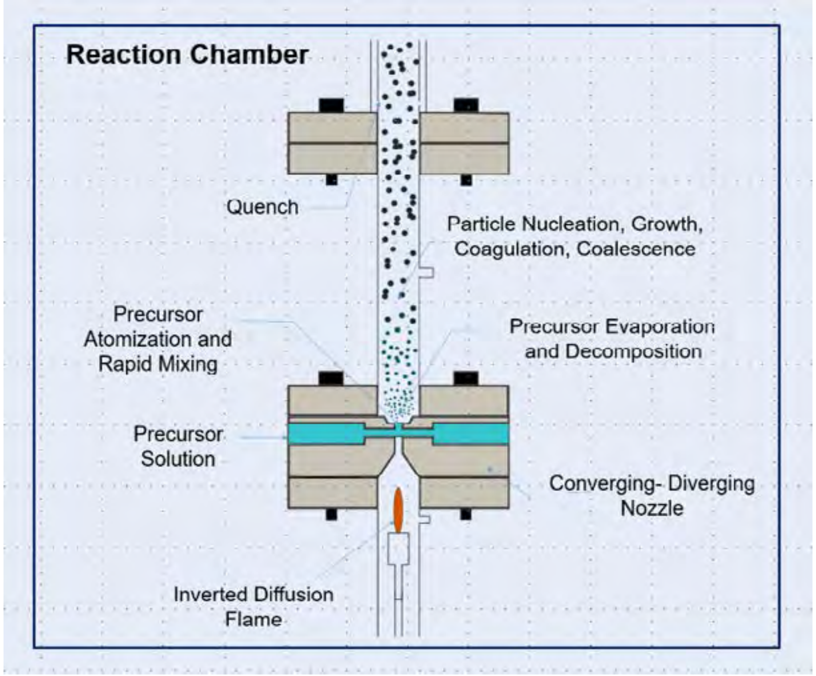

Figure 3: HTRJ reactor.

Particles prepared in the gas phase were collected as dry powders. For incorporation into polymer membranes, these nanoparticles must be stably dispersed in solvents that are also capable of dissolving the polymers of interest. The Pd alloy nanoparticles were suspended in toluene solvent and mixed with 5.0 wt% PBI in dimethylacetamide (DMAc) solvent. The combined dual solvent system incorporating both the dissolved PBI and nanoparticles was sonicated, then placed on a plate or support and allowed to dry at elevated temperature and under vacuum. The mixed matrix PBI/Pd layer was created directly on a support structure of polydimethylsiloxane (PDMS) silicone on pure PBI support, all of which is underlain by stainless steel mesh. In Figure 4, a very thin mixed matrix layer only 900 nm thick with embedded nanoparticles is visible on the silicone gutter layer, with porous PBI support underneath. In this image, the mixed matrix layer is 58 wt% or 13 vol% of Pd nanoparticles (designated PBI-Pd-58/13). Syntheses have increased Pd nanoparticle content up to 70 wt%; the point depicted in red in Figure 2 shows performance properties of the 70 wt% Pd/PBI MMM.

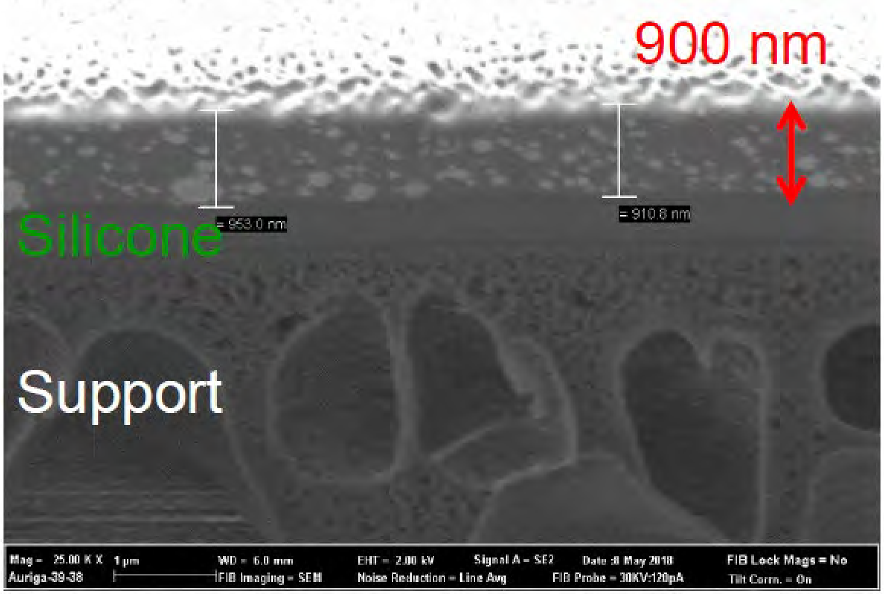

Figure 4: Cross-sectional scanning electron microscopy (SEM) of membranes.

Figure 5 shows the final laboratory-scale testing results for MMM permeability and selectivity for H_2/CO_2 separation. Behavior of optimized membranes at temperatures ranging from 150 to 225°C is shown for three loadings of nanoparticles

(22%, 46%, and 58% nanoparticles by weight). Note that the target performance region was attained with the PBI-PD-58/13 MMM.

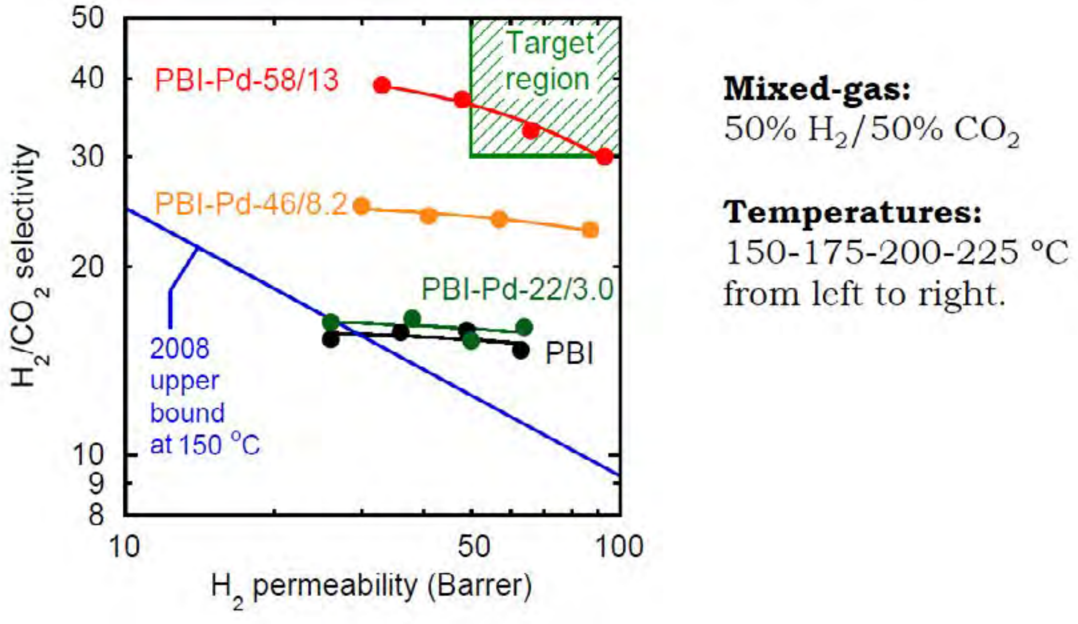

Figure 5: Effect of increasing Pd nanoparticle content on H_2/CO_2 separation in MMMs.

Also, stability of the MMMs in the presence of hydrogen sulfide (H_2S) and water (H_2O) was experimentally evaluated by measuring any changes of membrane permeability and selectivity with and without these species added to the simulated syngas mixtures. Satisfactory stability was observed in long-term laboratory-scale testing.

An important performance target of H_2 permeance of 500 GPU or greater at 150 to 200°C (with selectivity at least 30) had been set for this technology. Figure 6 shows the laboratory-scale permeances attained in this project (red) for a 70-nm thin-film MMM and various other competing H_2 separation membranes' permeance performance for comparison. Note that a thin-film MMM at 230°C would have more than adequate selectivity; however, with permeance of 400 GPU, it does not attain the target field.

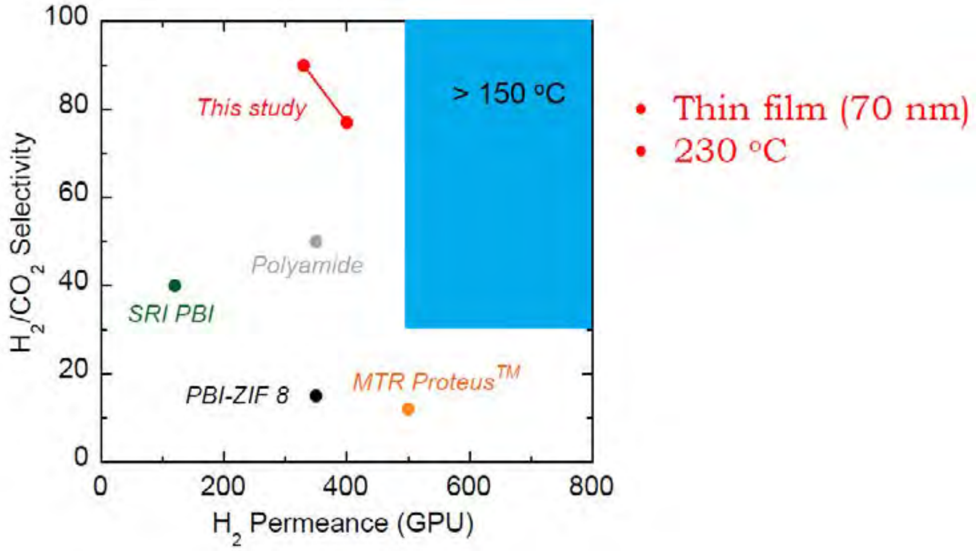

Figure 6: Hydrogen permeance target performance.

SUNY and Membrane Technology and Research Inc. (MTR) investigated behavior of the MMMs in a real syngas environment by testing of field stamps. This testing was conducted at the University of Kentucky's Center for Applied Energy Research (CAER), using syngas from the opposed multi-burner entrained flow coal gasifier at CAER. Samples were of large enough area to allow enough permeate gas flow rate for gas chromatography analysis (e.g., one stamp was about 3 cm^2 in area). Testing syngas flow rate was about 40–50 standard liters per minute (slpm), with test duration ranging from 23–40 hours. Syngas composition and conditions were approximately as follows:

TABLE 1: SYNGAS COMPOSITION FOR FIELD TESTING

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S + COS
65-115	104	17	20	0	40	20	2	149

Technical problems limited the field syngas temperature to 40°C (104°F)—a much lower value than intended.

Following exposure to syngas in the field, two samples were evaluated at the laboratory to measure any changes in permeability and selectivity for H_2/CO_2 separation. Gas separation performance of the samples before and after the field test is shown below. All the tests were conducted in mixed gas ($H_2:CO_2 = 50:50$) at 100 pounds per square inch gauge (psig). Significant decreases in gas selectivity were observed, stemming from decreases in H_2 permeance, increase in CO_2 permeance, or both.

TABLE 2: GAS SEPARATION PERFORMANCE OF THE SAMPLES BEFORE AND AFTER FIELD TESTING

Samples	Temp (°C)	H_2 Permeance (GPU)	CO_2 Permeance (GPU)	H_2/CO_2 Selectivity
#32 Before	150	146	3.4	42
#32 After	150	114 9	9.3	12
#23 Before	150	124	2.6	48
#23 After	60	7.5	1.3	5.8

TABLE 3: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymers	
Materials of Fabrication for Support Layer	—	polysulfone, polyethersulphone, etc.	
Nominal Thickness of Selective Layer	µm	0.1–0.2	0.1
Membrane Geometry	—	Flat sheet or hollow fiber	Flat sheet
Maximum Trans-Membrane Pressure	bar	50	50
Hours Tested without Significant Degradation	—	1 month	3 weeks
Manufacturing Cost for Membrane Material	\$/m^2	10-50	20-50
Membrane Performance			
Temperature	°C	100-300	250
H_2 Pressure Normalized Flux	GPU	200	500
H_2/H_2O Selectivity	—	0.1-0.5	—
H_2/CO_2 Selectivity	—	20	30
H_2/H_2S Selectivity	—	10-20	20
Sulfur Tolerance	ppm	50	10
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	spiral-wound modules	
Packing Density	m^2/m^3	1,000-5,000	
Shell-Side Fluid	—	syngas	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
H_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10-6 cm3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10-6 kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Barrer – Gas permeability unit of membrane selective materials, 10^{-10} cm^3 (STP)/(cm^2 s cm Hg).

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Resistant to water, high-pressure CO_2. However, the effects of sulfur and carbon monoxide (CO) on gas separation properties are to be determined.

Syngas Pretreatment Requirements – Sulfur removal and temperature adjustment.

Membrane Replacement Requirements – Not determined.

Waste Streams Generated – None identified.

Process Design Concept – Not determined.

technology advantages

- Synergism created by incorporating Pd in a polymer membrane, taking advantage of the well-understood properties and performance of PBI in membrane gas separations with the extremely high H_2 selectivity and permeability of Pd.
- Cost savings over pure Pd membranes, using relatively little expensive Pd metal, but still taking advantage of its H_2 sorption properties and stability against sulfur compounds.
- Good processability derived from polymer-based materials for the fabrication of the industrial thin-film composite membranes.

R&D challenges

- Membrane stability at operating conditions (elevated pressure and temperature).
- Loss of gas separation performance of membranes after exposure to sulfur-containing syngas.
- Fabrication of thin-film composite membranes consistently to specification and without defects.
- Scaled-up production of high-purity Pd nanoparticles and improving process yield.
- Attaining target region of selectivity versus permeability in MMMs.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

The project was completed at the end of 2019. Mixed matrix materials with superior H_2/CO_2 separation properties, and polymers and nanomaterials with promising H_2/CO_2 separation properties, were identified and prepared. Laboratory-scale testing of MMM-based membranes was completed, from which adequate H_2/CO_2 selectivity, targeted gas permeability, and stability in the presence of simulated syngas was confirmed. Field testing of membrane samples in actual coal syngas was completed, with before and after gas separation performance quantified; H_2/CO_2 selectivity fell by at least a factor of 4, suggesting challenges remain with membrane durability in exposure to realistic syngas conditions.

available reports/technical papers/presentations

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen (H_2) Purification and Carbon Dioxide (CO_2) Capture,” Final Report, Haiqing Lin, Ph.D. and Associate Professor, The U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, April 23, 2020. *https://www.osti.gov/servlets/purl/1603097*

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture,” presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Mixed-Matrix-Membranes.pdf*

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture,” presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-SUNY-Sorption-Enhanced-Mixed-Matrix-Membranes.pdf*

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture,” presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/2018-01/H-Lin-UB-Enhanced-Mixed-Matrix-Membranes.pdf*

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture,” presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File Library/Events/2016/c02 cap review/3-Wednesday/H-Lin-UBuffalo-Sorption-Enhanced-Mixed-Matrix-Membranes.pdf*

“Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture,” project kickoff meeting presentation, Pittsburgh, PA, October 5, 2015.

L. Zhu, M. Swihart and H. Lin, Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane H_2/CO_2 separation, Energy & Environmental Science, 2018, DOI: 10.1039/c7ee02865b

L. Zhu, M. Swihart and H. Lin, Tightening nanostructure of PBI for membrane H_2/CO_2 separation, Journal of Materials Chemistry A, 5, 19914-19923, 2017, DOI: 10.1039/C7TA03874G

Lingxiang Zhu, Maryam Omidvar and Haiqing Lin. “Manipulating Polyimide Nanostructures via Crosslinking for Membrane Gas Separation,” Chapter 6 in Membranes for Gas Separation, pp. 243-270, World Scientific, Aug 11, 2017.

H. Lin, “Molecularly Engineering Membrane Materials for Separations through Enhanced Interactions: A Road Less Traveled,” Department of Chemical and Materials Engineering and Center of Membrane Science, University of Kentucky, Lexington, KY, March 1, 2017.

H. Lin et al., “CO2-selective membranes for hydrogen production and CO2 capture – Part I: Membrane development,” Journal of Membrane Science, Volume 457, 149-161 (2014).

Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture

primary project goal

Membrane Technology and Research, Inc. (MTR) and partners Susteon and the Energy and Environmental Research Center (EERC) are maturing a technology based on a novel, hydrogen (H_2)-selective, multi-layer composite polymer membrane called Proteus™ for use in the separation of H_2 from post-shifted syngas. Project work is focused on the goal of scaling-up a second-generation Proteus membrane, including the fabrication of high-temperature prototype modules using second-generation (Gen-2) membranes and validating module performance in laboratory tests, followed by designing, constructing, and installing a prototype test system at EERC for parametric and lifetime testing of the modules with actual coal-derived syngas.

technical goals

- Optimize the Gen-2 Proteus membrane and develop modules capable of operation up to 200°C.
- Demonstrate membrane module performance while processing coal-derived syngas during a field test at EERC by demonstrating an H_2/carbon dioxide (CO_2) selectivity = 30 and recovering 2.5 lb/h H_2 at 75% purity at a syngas flow rate of 20 lb/h.
- Advance the Gen-2 Proteus membrane pre-combustion membrane capture technology from Technology Readiness Level (TRL) 4 to TRL 5.
- Optimize processes for integrating membrane modules into the integrated gasification combined cycle (IGCC) process with carbon capture (including evaluating sulfur treatment options), showing the potential via a techno-economic analysis (TEA) to reduce the cost of capture by more than 30% compared to Selexol.

technical content

MTR has been developing composite membranes for application in pre-combustion carbon capture where essential membrane characteristics include high H_2/CO_2 selectivity and high H_2 permeance rates. The MTR composite membrane for high temperature H_2 separation is called Proteus. Figure 1 illustrates the membrane structure and some characteristic composite membrane layers. Note that the key to competitive industrial performance is a very thin selective layer, which is required to allow high gas fluxes (or permeances) for given membrane surface areas.

program area:

Point Source Carbon Capture

ending scale:

Bench Scale

application:

Pre-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Composite Polymeric Membranes for CO_2 Capture from Coal Syngas

participant:

Membrane Technology and Research, Inc.

project number:

FE0031632

predecessor projects:

FE0001124

NETL project manager:

Carl Laird
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Jay Kniep
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partners:

Susteon Inc.; Energy and Environmental Research Center

start date:

10.01.2018

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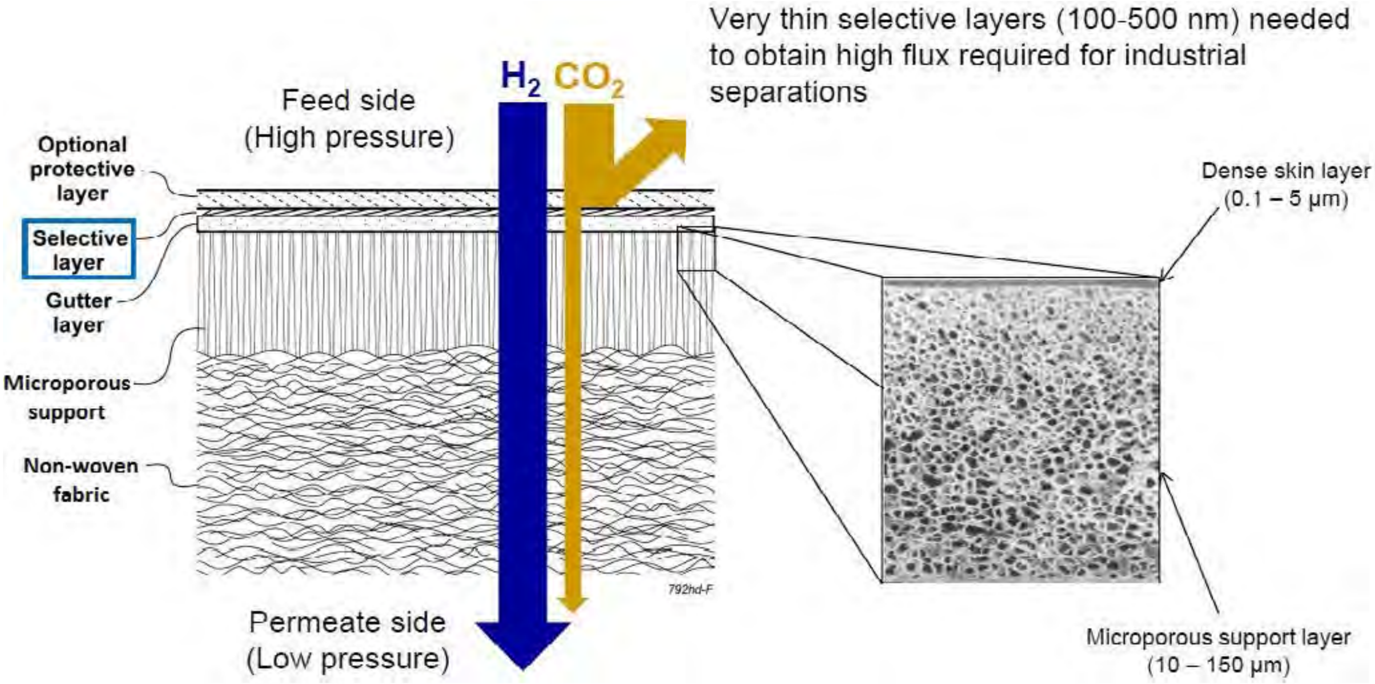

Figure 1: Proteus membrane multi-layer composite structure.

The H_2-selective Proteus membranes were first developed by MTR in work funded by the U.S. Department of Energy (DOE; DE-FE0001124). The first-generation membrane (Gen-1 Proteus) had an upper temperature limit of 150°C. Semi-commercial modules made from this membrane demonstrated stable operation for extended periods in the presence of sulfur and other contaminants in slipstream tests of actual coal-derived syngas from an air-blown gasifier at the National Carbon Capture Center (NCCC). By the end of testing in 2017, Gen-1 Proteus was evaluated in more than 15 different gasification campaigns accumulating 5,500 hours of run time for membrane stamps or lab-scale modules and 3,625 hours for semi-commercial modules at NCCC.

The subsequently developed Gen-2 Proteus has a higher temperature limit compared to the Gen-1 membrane (200°C versus 150°C), which allows for better heat integration into pre-combustion processes. The Gen-2 membrane also has improved H_2/CO_2 selectivity compared to the Gen-1 membrane, with an average value of 32 measured in membrane stamp testing at NCCC (compared to 15 to 20 for Gen 1 in the same tests). A new membrane treatment technique has been developed that improves the membrane H_2/CO_2 selectivity; the optimized membrane has achieved a selectivity of 37, which exceeds the project success criteria of 30. This improved selectivity reduces energy use and the required purification equipment size, thereby lowering operating and capital expenses.

To highlight the improved permeation performance of the Gen-2 Proteus membrane, Figure 2 compares the selectivity and permeance of this membrane with other polymers on a Robeson tradeoff plot.

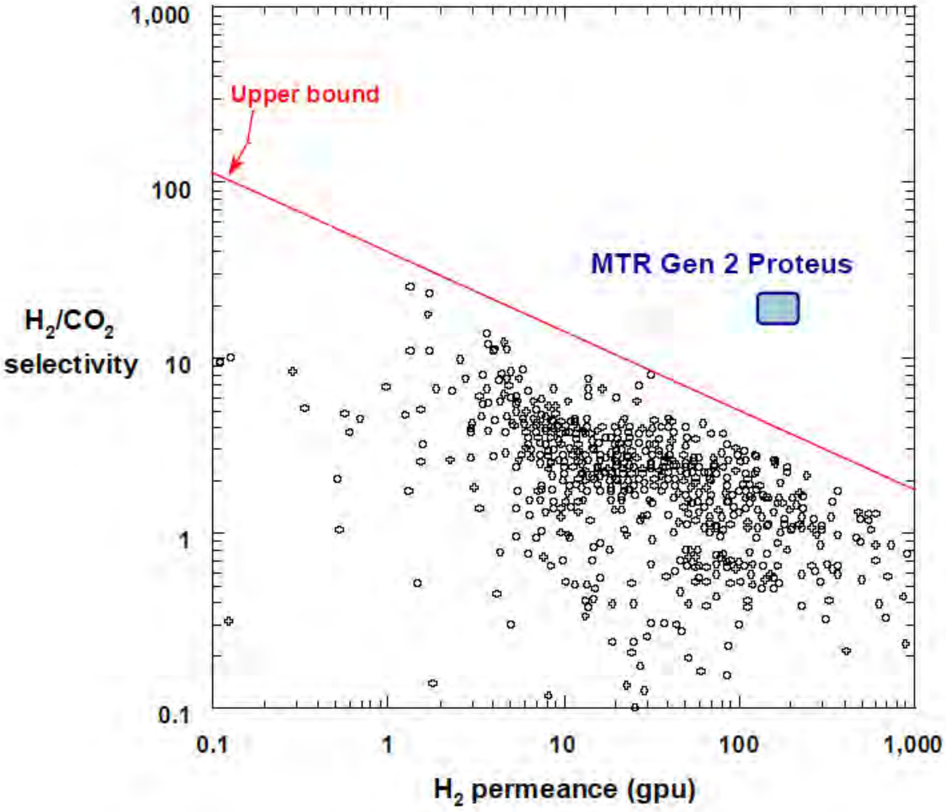

Figure 2: Robeson plot with Gen-2 Proteus membrane performance.

MTR has thoroughly tested the Gen-2 Proteus membrane to determine if all performance targets have been met. The membrane was both temperature- and pressure-cycled to verify robustness; gas permeance values were found to be very stable over multiple heating and cooling cycles, as shown in Figure 3. In addition, the membrane was pressure-cycled in nitrogen between 100 and 1,000 pounds per square inch gauge (psig); nitrogen permeance increased to 5 gas permeation units (GPU) at high pressure and consistently returned to 2 GPU at low pressure. The optimized Gen-2 Proteus membrane retained its high selectivity after operational cycling, showing the robustness of the membrane.

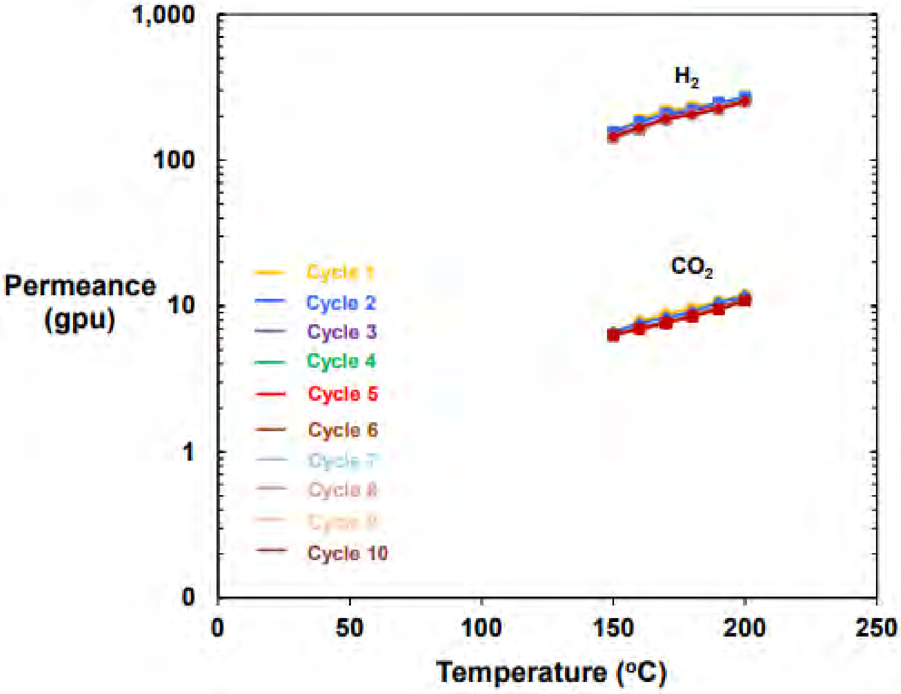

Figure 3: Gen-2 Proteus membrane temperature cycling results.

Process Scenarios

A simplified process flow diagram for carbon capture with membranes in an IGCC power cycle is depicted in Figure 4. Coal is converted by oxygen-based pressurized gasification resulting in a raw syngas. This syngas is shifted via the water-gas shift (WGS) reaction to produce syngas consisting mostly of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane capture unit. The high-partial pressure driving force, combined with a nitrogen (N_2) sweep on the lower-pressure permeate side of the membrane, causes selective H_2 permeation into the N_2 sweep, which serves as fuel gas in a combustion turbine. The high-pressure membrane retentate is enriched in CO_2 that can then be further purified, compressed, and sent to storage.

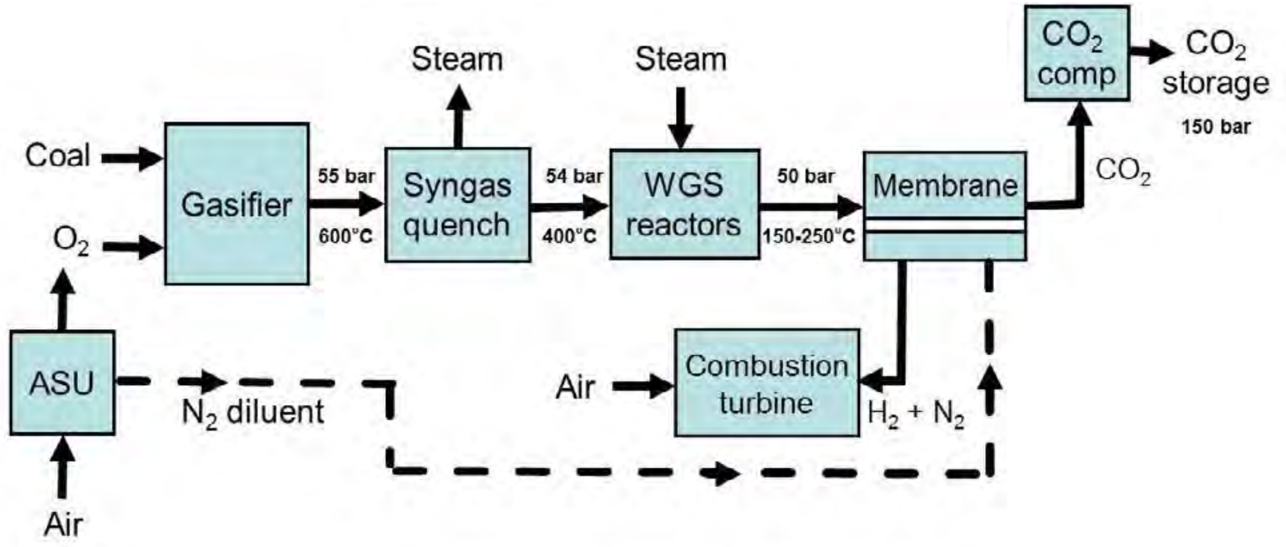

Figure 4: Overall process design for the pre-combustion capture membrane system.

Figure 5 shows additional process details for the MTR pre-combustion CO_2 capture process. After using the Proteus membrane to recover H_2, a series of steps are used to purify CO_2. These steps include (1) sulfur removal, (2) gas drying, (3) refrigeration to produce liquid CO_2, (4) additional CO_2 recovery with the MTR Polaris™ membrane, and (5) pumping liquid CO_2 to storage pressure. The CO_2 purity can be readily increased to greater than 99% in this process. In comparison to a baseline case (GE Gasifier with two-stage Selexol [i.e., Case 2 of DOE Bituminous Baselines Study]), prior studies showed that the MTR membrane process provides a 27-megawatt-electric (MWe) net power improvement and a 7.4% lower cost of energy (COE) using Gen-1 Proteus membrane properties. Both the warm (H_2 membrane) and cold (CO_2 membrane) portions of the MTR process have been validated in independent skid field tests at NCCC.

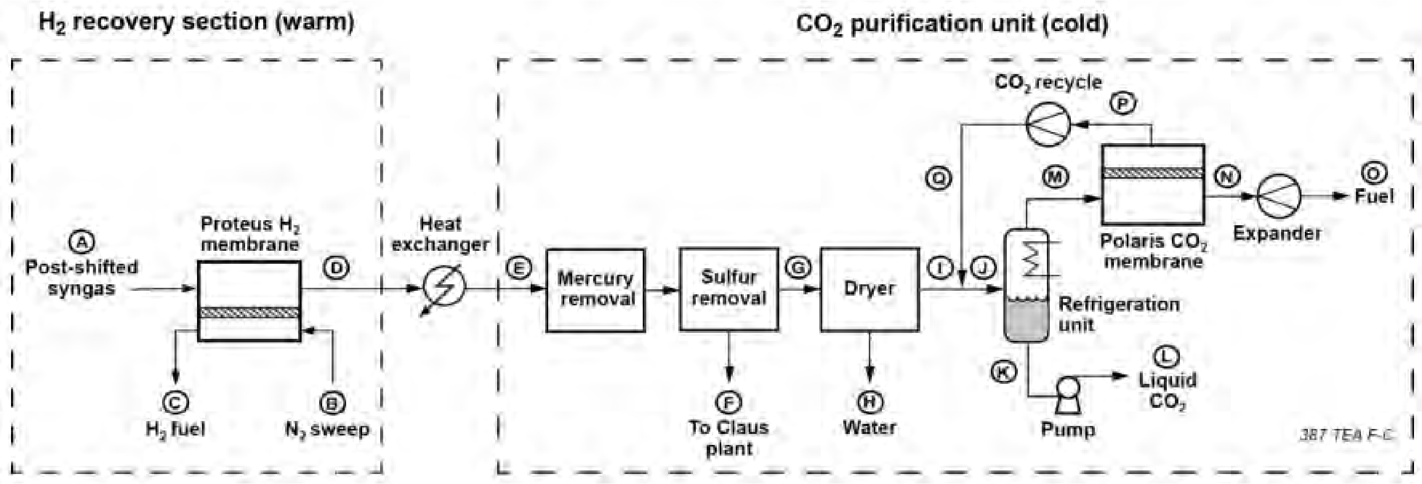

Figure 5: MTR dual-membrane process for H_2 recovery and CO_2 capture in IGCC power generation.

For industrial applications, Proteus membranes can be packed into spiral-wound membrane modules, a commonly used module design for commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 6 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, allowing separated H_2 to be swept by N_2 on the permeate side and CO_2 retained on the feed site to flow through the device. In bench-scale work, modules have membrane area of 1 to 4 m^2, and accommodate gas flow of about 50 lb/h. Commercial modules have membrane area of 20 to 50 m^2, and accommodate gas flow of about 500 lb/h.

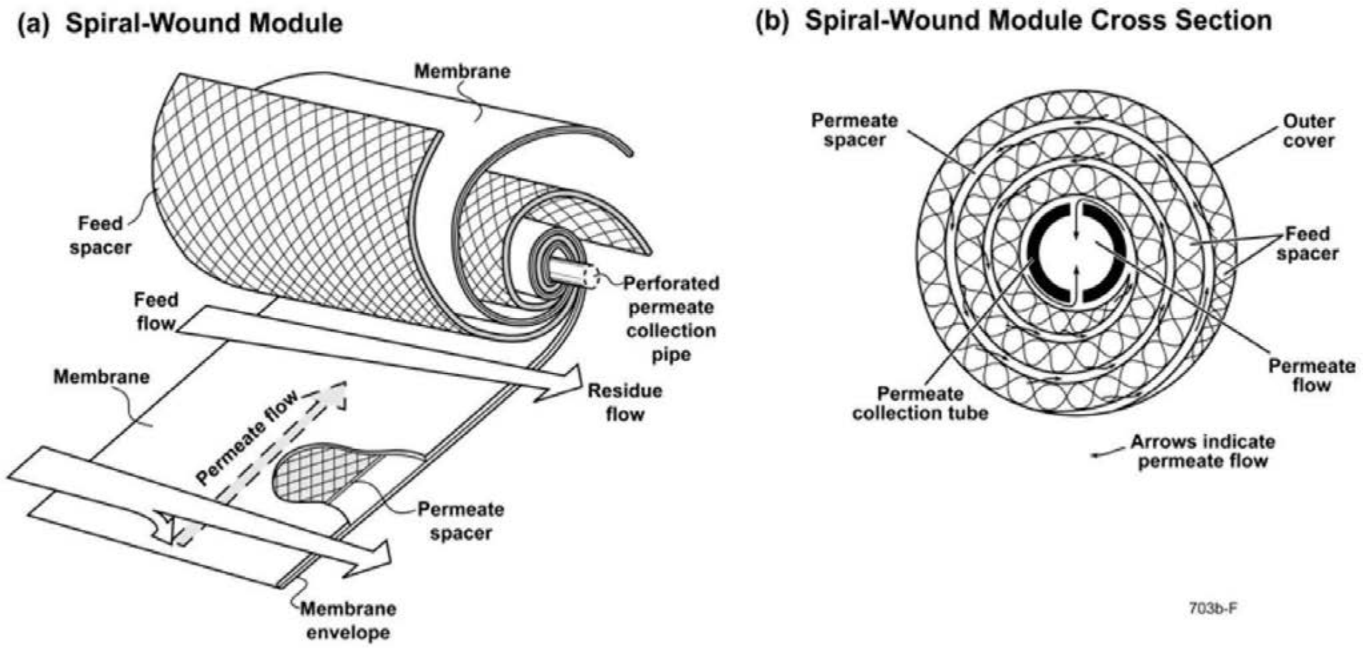

Figure 6: Schematic diagram of a spiral-wound membrane module.

Bench-Scale Field Testing

MTR constructed a bench-scale testing unit incorporating semi-commercial-scale spiral-wound modules. The bench-scale unit was deployed in field-testing at EERC in 2021. EERC's oxygen-blown fluidized bed gasifier supplied syngas for the testing; syngas conditions were as follows:

- 300 to 500 psig gas pressure.
- 30 to 35% H_2; 40 to 50% CO_2.
- Up to 3,000 parts per million (ppm) hydrogen sulfide (H_2S).

A full parametric test matrix of temperature and feed syngas pressures was completed in the testing. For assessment of operational robustness, modules were temperature-cycled up to a simulated process upset condition of 215°C at a syngas pressure of 300 psig. Initial and final 170°C H_2 permeance values were in excellent agreement with the MTR laboratory mixed gas value of 255 GPU, as shown in Figure 7. Overall, testing findings were encouraging, with post-field test examination of the modules finding no membrane pin-hole leaks, good membrane/spacer compatibility and spacers condition, glue lines intact, and no evidence found of module degradation due to high-temperature syngas exposure.

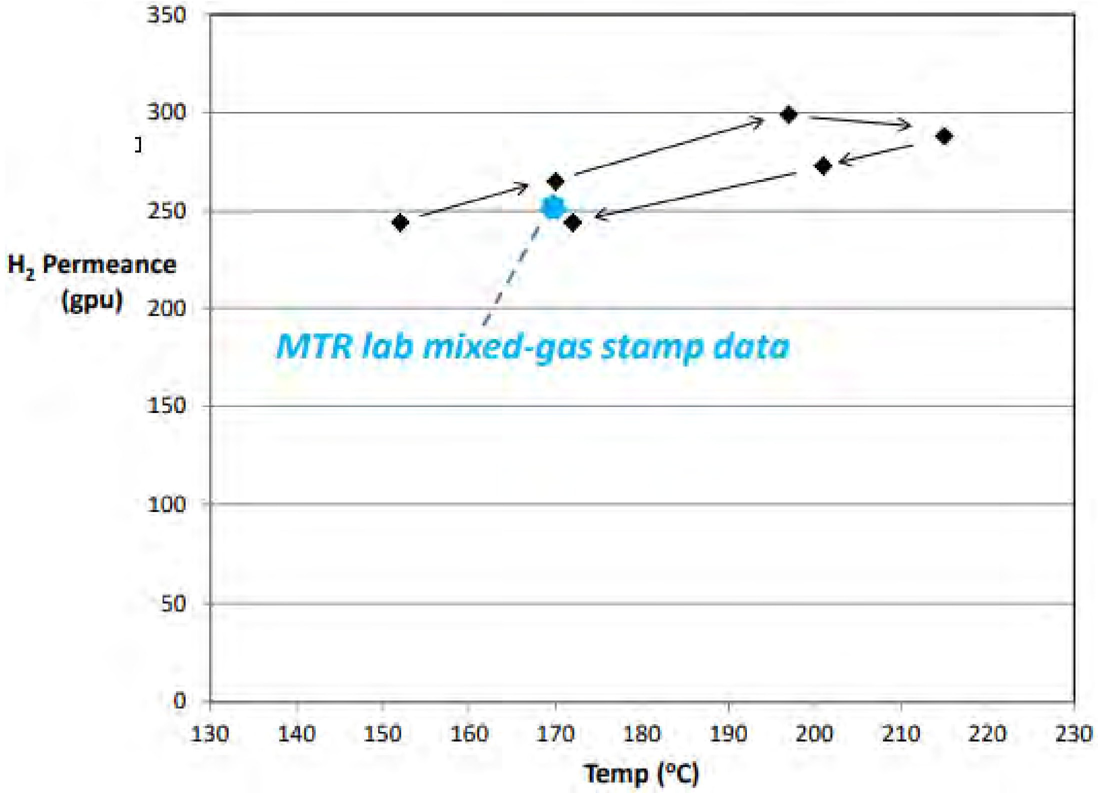

Figure 7: Influence of temperature on H_2 permeance during EERC field test of the Gen-2 Proteus module.

Technoeconomic Analysis

The TEA for this project is assuming the configuration of the reference plant B5B found in the Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Rev. 4. Gen-2 Proteus membrane performance numbers being used in the TEA were validated during a bench-scale field test (TRL-5) at the EERC with an oxygen-blown fluidized bed gasifier as the coal-derived syngas source.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymers	
Materials of Fabrication for Support Layer	—	Proprietary polymers	
Nominal Thickness of Selective Layer	µm	< 1 micron	< 1 micron
Membrane Geometry	—	Flat sheet	Flat sheet
Maximum Trans-Membrane Pressure	bar	75	75
Hours Tested without Significant Degradation	—	1 month	3 months
Manufacturing Cost for Membrane Material	$\$/m^2$	500	250
Membrane Performance			
Temperature	°C	200	200
H_2 Pressure Normalized Flux	GPU or equivalent	275	200
H_2/H_2O Selectivity	—	0.4	0.4
H_2/CO_2 Selectivity	—	37	30
H_2/H_2S Selectivity	—	>50	50
Sulfur Tolerance	ppm	Inert to Sulfur	Inert to Sulfur
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	Syngas	
Syngas Gas Flowrate	kg/hr	717,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 99.5 152.7	
H_2 Recovery, Purity, and Pressure	%/%/bar	99.4 44 % in N_2 as fuel 30	
Pressure Drops Shell/Tube Side	bar	feed: 1 /sweep: 1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	15	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Proteus membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The MTR membranes and membrane module components are compatible with the species found in coal-derived syngas. This is one of the major findings from syngas field tests conducted at NCCC between 2009 and 2017 for both the Polaris™ (5,200 cumulative hours online) and Proteus (9,125 cumulative hours online) membranes.

Syngas Pretreatment Requirements – The MTR pre-combustion CO_2 capture membrane process design does not require syngas pretreatment.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – No additional waste streams are generated when adding the MTR pre-combustion CO_2 capture system to an IGCC process. Similar to the stand-alone IGCC process, water removed from the MTR process can be recycled to process demand and the removed sulfur species can be sent to a Claus plant for processing. The high-purity CO_2 product can be used for enhanced oil recovery or other industrial applications.

Proposed Module Design – Spiral-wound modules; see Figure 6.

The pressure, temperature, and composition of the gas entering the membrane module are as follows:

		Composition						
Pressure	Temperature	vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
740	392	40.73	1.19	0.01	0.77	55.79	0.18	6230

technology advantages

- The Proteus membrane allows separation of H_2 from syngas at elevated temperatures. This ability to operate warm/hot reduces the need for heat exchange (e.g., membrane modules operate at a higher temperature than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and water condensation).
- A membrane system does not contain moving parts or involve chemical reactions, making it simple to operate and maintain.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- The membrane capture system permeates water in syngas (increase mass to turbine and reduces CO_2 dehydration costs).
- Membrane modules downstream from pressurized WGS maintain CO_2 effluent at pressure; therefore, less compression of CO_2 product is required compared to conventional acid gas removal processes.
- The proposed N_2 sweep on the H_2 permeate side increases the partial pressure driving force for separation and decreases the required membrane area.

R&D challenges

- Countercurrent sweep module design could result in several potential inefficiencies, including sweep-side pressure drop, concentration polarization, poor utilization of the membrane area, and non-countercurrent flow patterns.
- Feed and permeate side pressure drops could lead to excessive energy losses if modules are not designed properly.
- Membrane module cost reductions will be needed if the technology is to become economically viable.
- Scale-up and integration issues are possible given the large number of modules needed to service a 550-MWe plant.

status

A second-generation Proteus membrane has been made with performance that exceeds H_2/CO_2 selectivity targets. The membrane was incorporated in near-commercial-scale robust membrane modules, which were deployed in a bench-scale field-test skid for evaluation of capture performance on oxygen-blown, gasifier-produced, high-temperature syngas at EERC. The membrane and module were found to perform robustly and maintained durability after exposure to the sulfur-containing syngas. Field test data analysis has been completed and the results are currently being incorporated into the final TEA.

available reports/technical papers/presentations

"Bench-Scale Development of a Transformative Membrane Process For Pre-Combustion CO2 Capture," presented by Jay Kniep, Membrane Technology and Research, Inc., DOE NETL Virtual Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Kniep.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture," Membrane Technology and Research, Inc., Project Budget Period 2 Meeting Presentation, September 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=10546&filename=Bench-Scale+Development+of+a+Transformative+Membrane+Process+for+Pre-Combustion+CO2+Capture.pptx.*

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture," presented by Jay Kniep, Membrane Technology and Research, Inc., 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Precombustion-Membrane.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture," presented by Jay Kniep, Membrane Technology and Research, Inc., 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Kniep-MTR-Transformative-Membrane-Process.pdf*.

"Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO2 Capture," Project kickoff meeting presentation, December 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10543&filename=Bench-Scale+Development+of+a+Transformative+Membrane+Process+for+Pre-Combustion+CO2+Capture+.pdf.*

"Novel Polymer Membrane Process for Pre-combustion CO2 Capture from Coal-fired Syngas," Final Report for DE-FE0001124, Membrane Technology and Research, Inc., December 2011. *https://www.osti.gov/servlets/purl/1080044.*

Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture

primary project goal

SRI's overall goal is to develop a technically and economically viable carbon dioxide (CO_2) capture system based on a high-temperature polybenzimidazole (PBI) polymer hollow-fiber membrane separation technology. This is intended for deployment at elevated temperatures to separate hydrogen (H_2) and CO_2 in shifted syngas, enabling pre-combustion carbon capture in integrated gasification combined cycle (IGCC) power plants. The project goals are to extend previous work on PBI hollow-fiber membranes to further evaluate second-generation (Gen-2) fibers having improved selectivity through the development and field testing of Gen-2 PBI-based membrane modules on actual coal-derived syngas from an oxygen-blown gasifier.

technical goals

- Produce at least 100 kilometers of Gen-2 fibers that provide an H_2/CO_2 selectivity of about 40 and H_2 permeance of 80–120 gas permeation units (GPU) at greater than 150°C at a 150 pounds per square inch (psi) pressure differential.
- Modify the existing 50-killowatt-thermal (kWth) bench-scale test skid (fabricated and used in FE0012965) with Gen-2 hollow-fiber modules of 4- to 6-inch diameter, and complete bench-skid acceptance testing for 50 hours achieving H_2/CO_2 selectivity greater than 35.
- Perform bench-scale testing at temperatures ≈225°C and up to a pressure of 30 bar under various operating conditions, including long-term steady-state conditions using actual coal-derived syngas (throughput equivalent to 50 kWth) from the entrained flow oxygen-fed gasifier at the University of Kentucky's Center for Applied Energy Research (CAER).
- Prepare techno-economic analysis (TEA) based on Gen-2 bench-scale testing results to re-evaluate technology performance to achieve DOE's pre-combustion capture targets.

technical content

SRI's PBI membrane-based technology is being developed for high-temperature pre-combustion separation of H_2 from shifted syngas, leaving a high-concentration, high-pressure CO_2-rich stream in the retentate and yielding a high H_2-content permeate stream. SRI's membranes consist of asymmetric hollow-fiber PBI (molecular structure of the polymer shown in Figure 1), which is chemically and thermally stable at temperatures up to 300°C and pressures up to 55 atmospheres (atm; 800 pounds per square inch gauge [psig]). PBI membranes are also sulfur tolerant. These characteristics permit the use of the PBI membrane for CO_2 capture downstream of a sour water-gas shift (WGS) reactor without

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
PBI Polymer Membrane for CO_2 Capture from Coal Syngas

participant:
SRI International

project number:
FE0031633

predecessor projects:
FC26-07NT43090; FE0012965

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Krista Hill
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principal investigator:
Indira Jayaweera
SRI International
indira.jayaweera@sri.com

partners:
Enerfex Inc.; PBI Performance Products; University of Kentucky Research Foundation

start date:
10.01.2018

percent complete:
95%

requiring further gas cooling before the PBI membrane, significantly increasing plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.

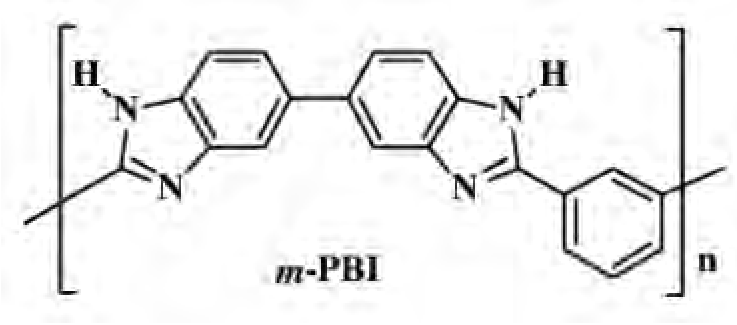


Figure 1: m-polybenzimidazole molecular structure.

Single-bore PBI-based hollow fibers have been shown to be highly durable, with near-constant levels of permeability and selectivity over the course of 330 days while in the presence of H_2, carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250°C. Therefore, PBI fiber modules can be successfully used in pre-combustion CO_2 capture applications.

PBI-based hollow fibers, as seen in various magnified views in Figure 2, offer a considerable advantage over coated stainless-steel tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1–0.5 micrometer separation layer (the dense layer). Ease of large-scale manufacturability, high packing density, and the cost are notable advantages of hollow-fiber membrane systems.

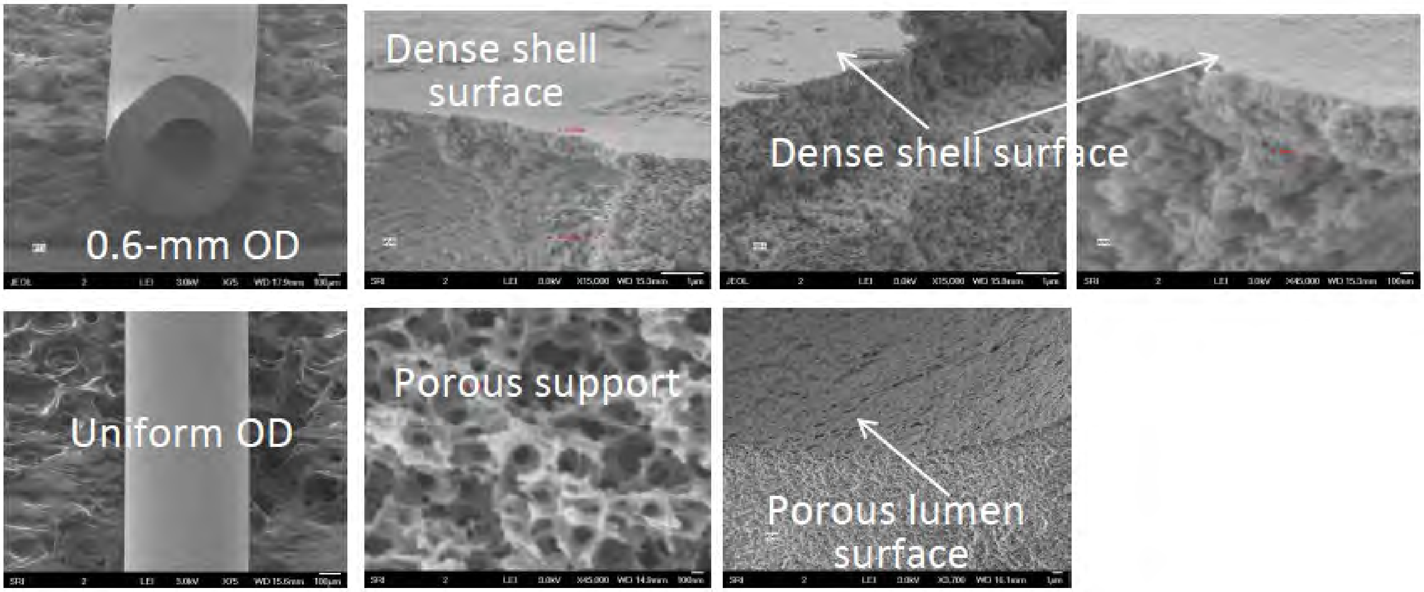


Figure 2: PBI hollow-fiber membranes and details of physical structure.

Fiber Fabrication and Modules

Hollow-fiber membrane fabrication is accomplished in a spinning line as depicted in Figure 3. An important part of technology maturation involves improvements in fiber spinning technology enabling an improved and robust spinning process that can be transferred to industry. Improvements in the spinning line have enabled use of multiple coagulation solvents, increased productivity (one-gallon reservoir size), process monitoring and data collection, precise flow controls and draw ratios, optimization of fiber diameter, and optimization of the fiber dense-layer thickness.

SRI has been improving its developed protocols to enable spinning dense layer hollow-fiber membranes that are less than 0.3-µm in thickness, with outer diameters (ODs) of 450–650 µm. Figure 2 includes photographs of a hollow-fiber membrane well within this range, with around 0.1-µm dense layer fibers having approximately 600-µm OD. Optimization of OD and dense layer has been supported through testing of more than 100 fiber bundles (1-inch). Fabrication of the Gen-1 hollow-fiber membrane with a very thin, dense layer (less than 0.3 µm) in kilometer lengths has been accomplished with very good reproducibility. In previous work, more than 100 kilometers of Gen-1 fibers have been spun for both Generon and SRI modules (4-inch diameter size fiber modules). In the latest work, more than 10 kilometers of the improved performance Gen-2 fibers have been produced so far for deployment in the new modules to be used in upcoming testing at the University of Kentucky's CAER. Performance parameters for the Gen-2 membranes are shown in Table 1.

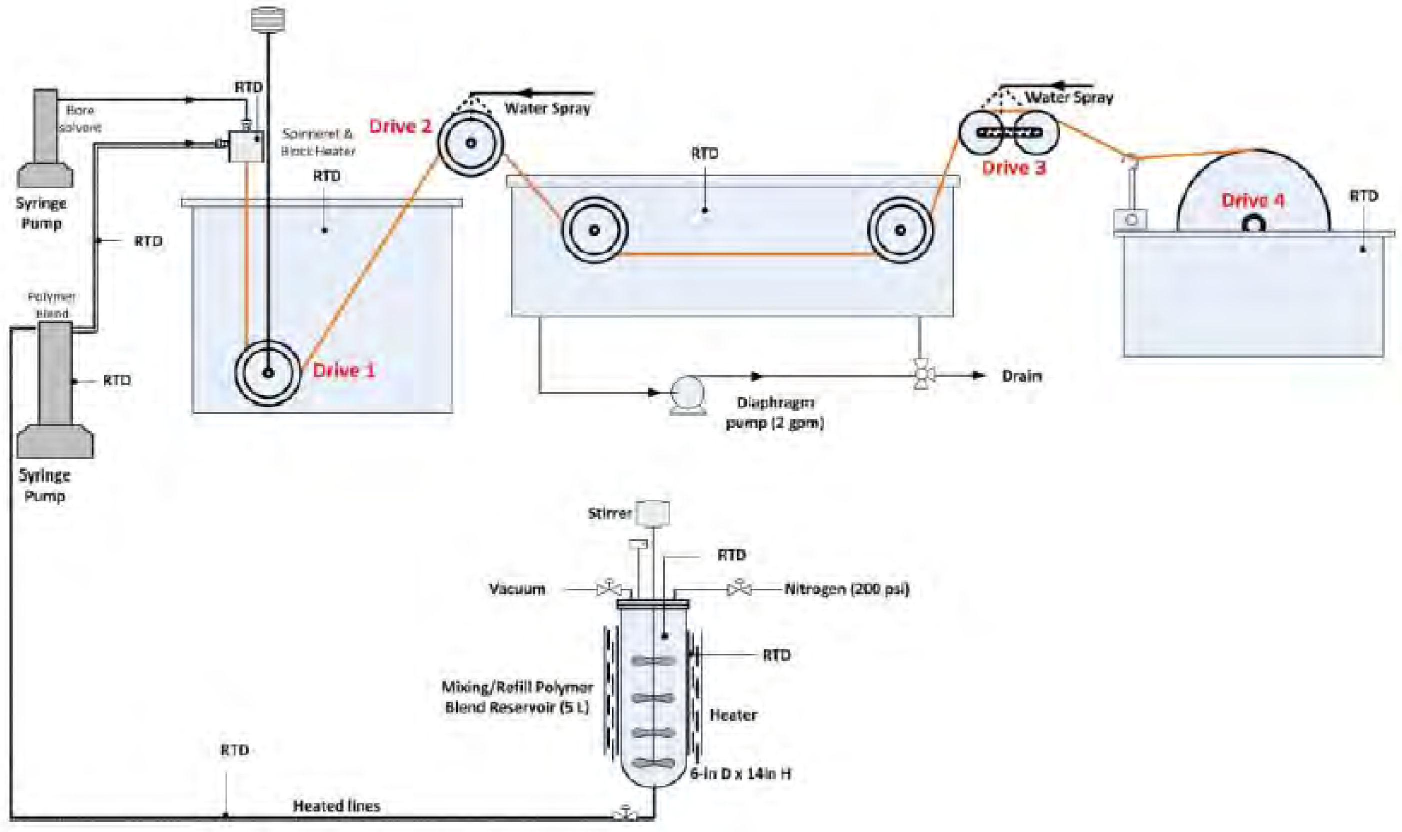


Figure 3: SRI hollow-fiber membrane spinning line.

Large bundles of hollow fibers are potted in tube sheet modules (currently in 4- or 6-inch diameters), which can then be assembled into larger-scale gas separation units/skid for process implementation. Figure 4 shows the cross-section of an actual 4-inch fiber module as fabricated at SRI (on the left); these are the type that had been incorporated in the bench-scale skid, which was deployed in past testing at the National Carbon Capture Center (NCCC) on a syngas slip stream. SRI fiber modules are designed for easy fabrication, easy handling, and easy drop-in replacement. A new tube sheet module design is being deployed (images on right side of Figure 4). These will enable faster module swapping and reduced gas bypass characteristics.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer		PBI	PBI
Materials of Fabrication for Support Layer		PBI	PBI
Nominal Thickness of Selective Layer	µm	0.3–2	<0.5
Membrane Geometry		hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	≈14	>20
Hours Tested without Significant Degradation	hr.	1,000	1,000
Manufacturing Cost for Membrane Material	$/m^2	30–80	TBD
Membrane Performance			
Temperature	°C	200–250	225

H_2 Pressure Normalized Flux	GPU or equivalent	80–120	80–120
H_2/H_2O Selectivity	—	<1	<1
H_2/CO_2 Selectivity (Dense layer thickness)	—	40 (>1 µm) and 22 (<0.3 µm)	40 (<0.3 µm)
H_2/H_2S Selectivity (Dense layer thickness)	—	>200 (>1 µm)	>200 (<0.3 µm)
Sulfur Tolerance	ppm	300	300
Type of Measurement		pure and mixed	mixed gases
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement		countercurrent	
Packing Density	m^2/m^3	>3,000	
Shell-Side Fluid		retentate or permeate	
Syngas Flowrate	kg/hr	22	
CO_2 Recovery, Purity, and Pressure	%/%/bar	TBD	
H_2 Recovery, Purity, and Pressure	%/%/bar	>98%, >49%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	<0.007/0.03	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	TBD	

*A commercial 4-inch module design with 200 µm bore diameter and 28–48 bar feed pressure was assumed.

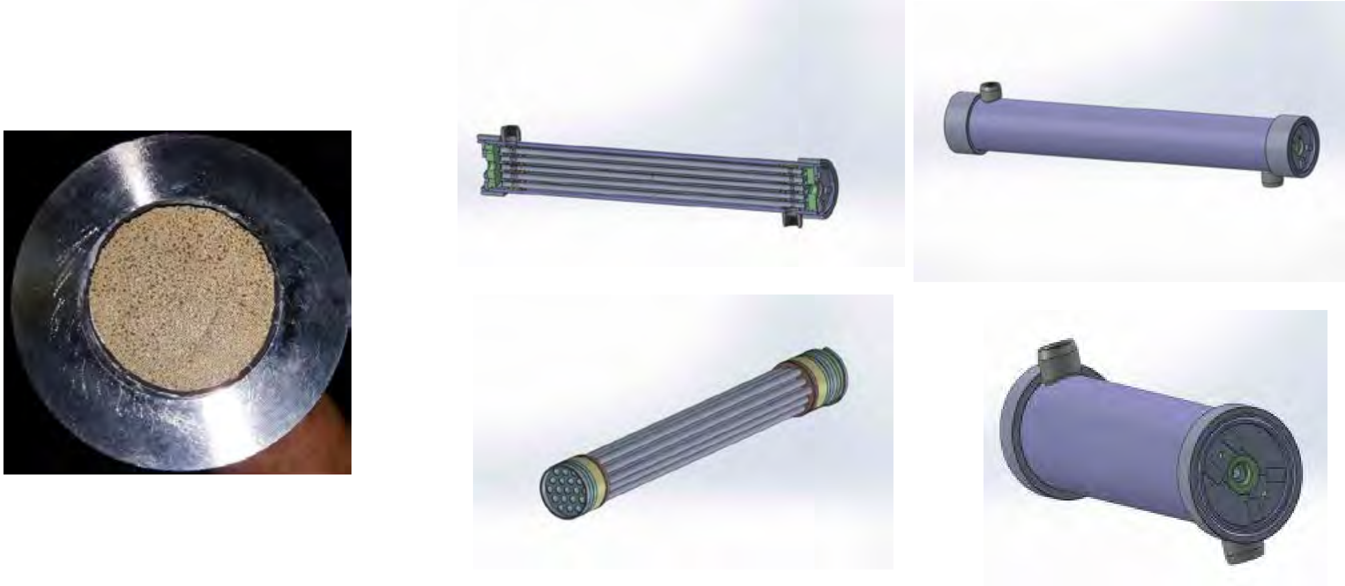


Figure 4: Potted module cross-section (left-most); new tube sheet module design (right).

Testing Results

Results of testing PBI modules at NCCC on air-blown gasifier syngas have established performance characteristics of both the Gen-1 and Gen-2 PBI modules. Specifically, membrane element TS-1 (consisting of SRI Gen-1 fibers having GPU ~150, H_2/CO_2 selectivity ~25 at 150°C) was tested for about 500 hours. Membrane element TS-2 (consisting of SRI Gen-2 fibers having GPU ~100, H_2/CO_2 selectivity ~40 at 200°C, and at 200 psi) was tested for 48 hours. Figure 5 plots selectivity results of various testing runs for both Gen-1 and Gen-2 testing campaigns. Selectivity of Gen-2 shows definite improvement with potential for superior performance at target operating temperatures of approximately 200°C. Taken with gas permeance measurements (Figure 6), the Gen-2 modules evidence significant performance advantages over Gen-1.

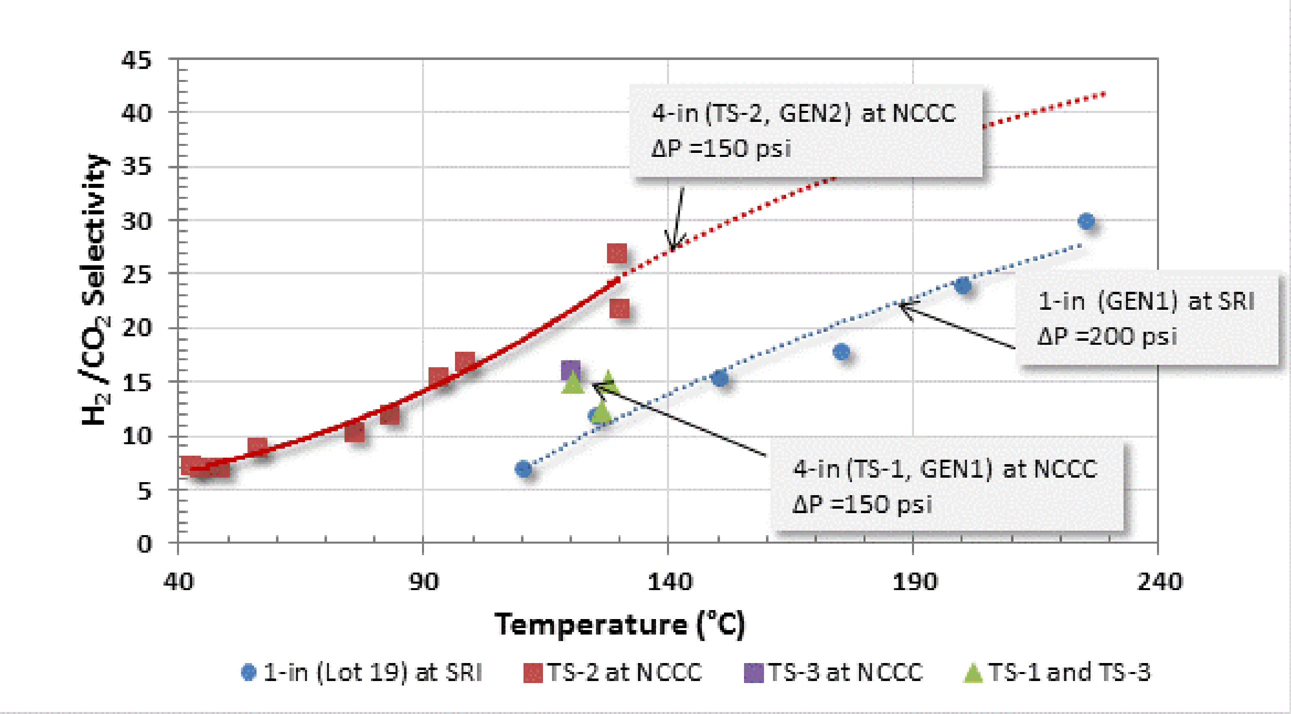


Figure 5: Comparison of measured H_2/CO_2 selectivity for Gen-1 and Gen-2 PBI modules.

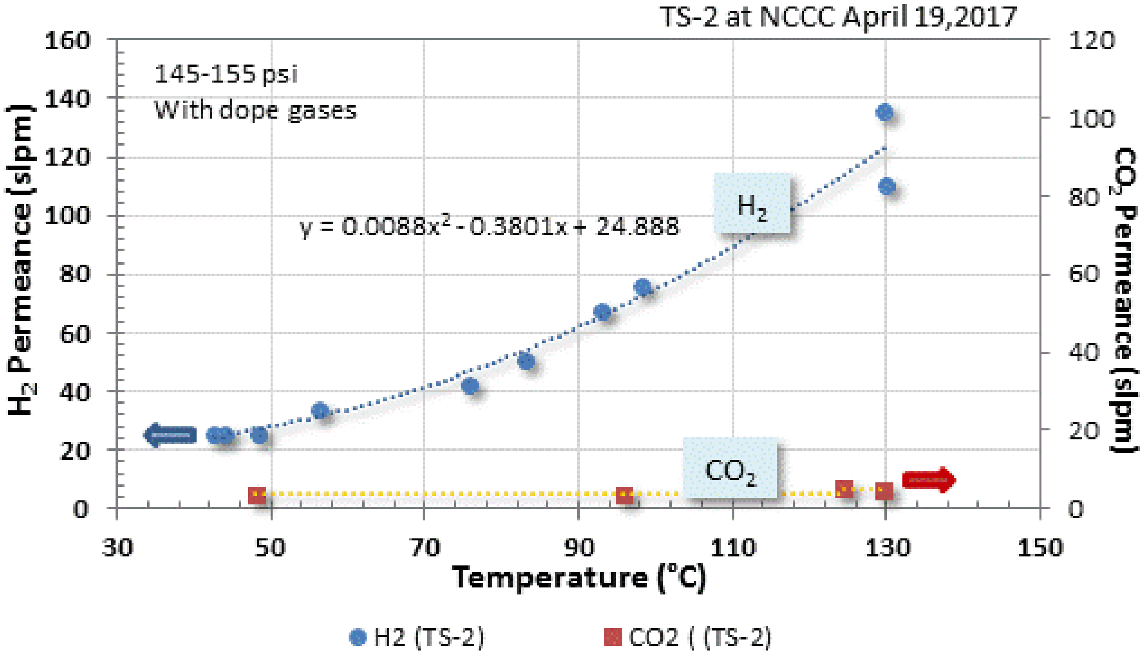


Figure 6: Measured H_2 and CO_2 permeances for the Gen-2 module at varying temperatures under a pressure differential of 145–155 psi.

Preliminary Techno-Economic Analysis Findings

SRI has previously made estimations of cost of electricity (COE) reductions that should be possible by application of the PBI membrane technology in process implementation in the context of an IGCC power plant cycle. From testing of Gen-1 and Gen-2 membranes, performance parameters have been quantified. Given expected Gen-1 and Gen-2 gas selectivities and different gas permeance assumptions, it is possible that the PBI membrane technology can meet National Energy Technology Laboratory (NETL) targets, assuming the membrane system has capital cost reductions that are expected to emerge in industrial-scale economies and savings associated with high levels of system optimization, which are anticipated as higher Technology Readiness Levels (TRLs) are attained. Current research and development (R&D) techno-economic data is shown in Table 2.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	\$32	<\$32
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/MWhr	\$75	TBD
Operating Expenditures	\$/MWhr	\$60	TBD
Cost of Electricity	\$/MWhr	\$135*	<\$135

* >99% hydrogen recovery with 90% CO_2 capture.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – PBI is resistant to acidic contaminants.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – Required frequency of membrane replacement to be determined.

Waste Streams Generated – Gaseous waste stream generated includes CO_2 and H_2S separated from the syngas. This stream will be further treated to remove H_2S.

Process Design Concept – Flowsheet/block flow diagram is shown in Figure 7. Note that the PBI hollow-fiber membrane is both a water and H_2 transporting membrane, so most water vapor/steam in the shifted syngas will segregate into the permeate stream along with the H_2.

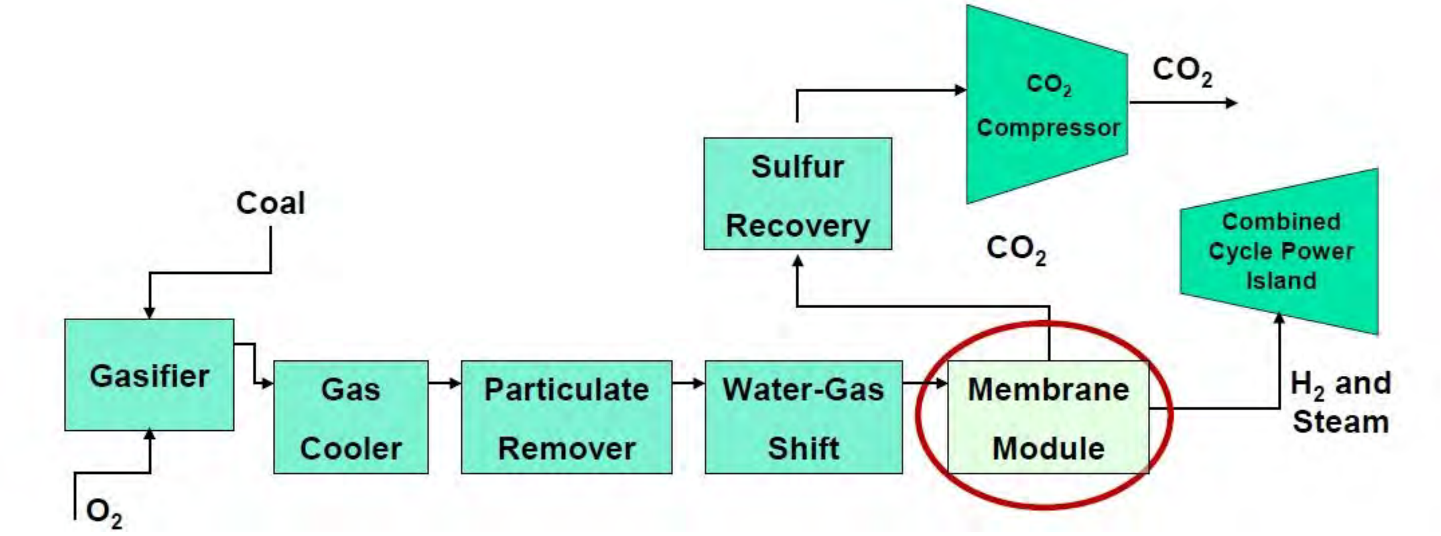
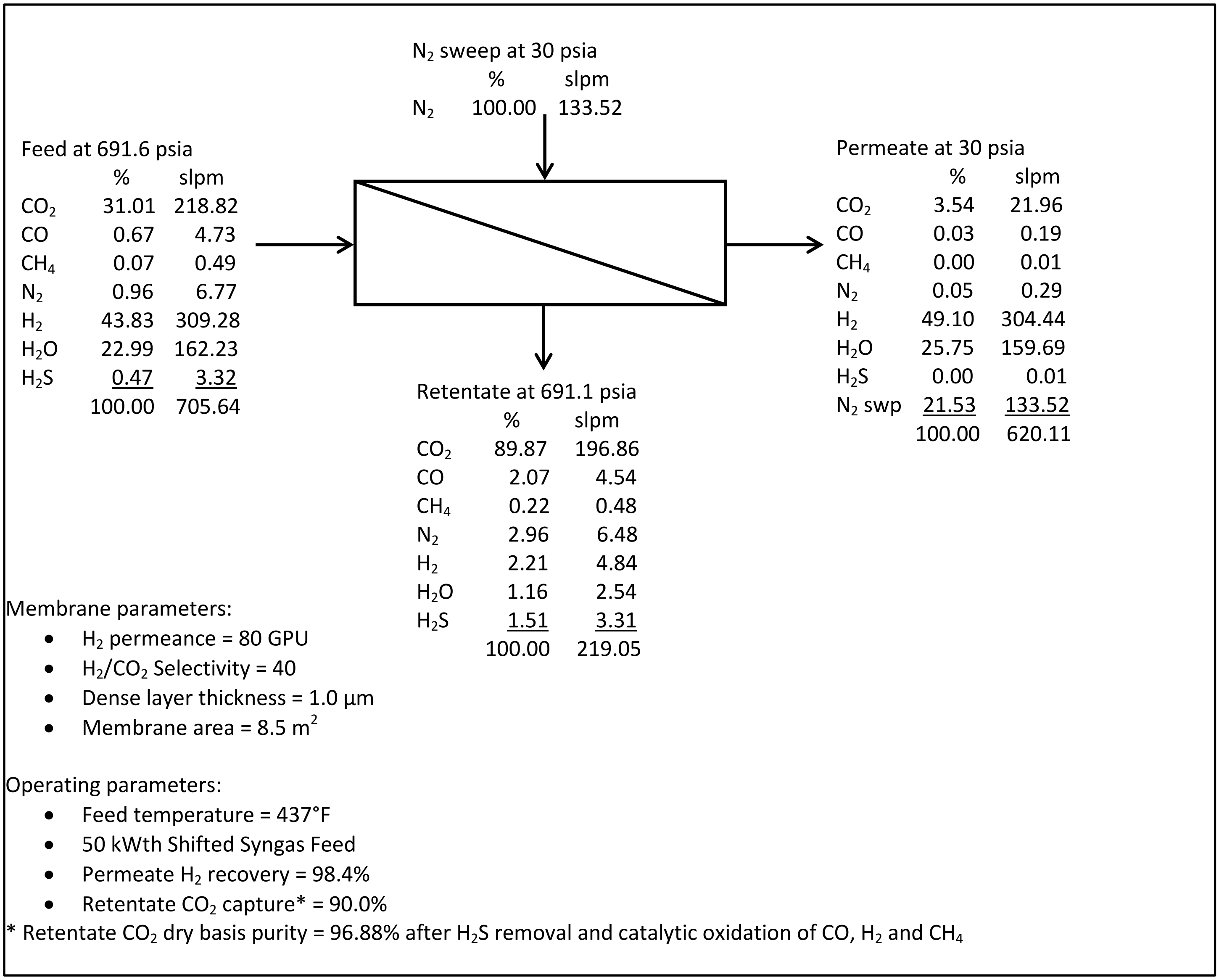


Figure 7: Flowsheet/block flow diagram showing PBI membrane module integration in the IGCC plant process.

Proposed Module Integration – Module design is tubular with 4-inch diameter and 36-inch length. Figure 8 shows the simulated module performance: the pressure, temperature, and composition of the gas entering the module, assuming H_2/CO_2 selectivity of 40. Note that the module feed gas is from an oxygen-blown gasifier with a shifted syngas feed to the membrane. In an oxygen-blown gasifier (assumed in TEA), the permeate recovers 98.4% of the feed H_2 and the retentate captures 90% of the feed CO_2. The retentate stream is further processed in a Claus plant to remove H_2S and a catalytic oxidizer to convert CO and CH_4 to CO_2 and H_2 to water (H_2O). The final retentate dry basis CO_2 purity is 96.88%.

The composition of the gas entering the module is shown below:

Pressure	Temperature	Composition						
		vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
691.1	437	31.01	0.67	0.07	0.96	43.83	22.99	0.47



N_2 sweep at 30 psia

	%	slpm
N_2	100.00	133.52

Feed at 691.6 psia

	%	slpm
CO_2	31.01	218.82
CO	0.67	4.73
CH_4	0.07	0.49
N_2	0.96	6.77
H_2	43.83	309.28
H_2O	22.99	162.23
H_2S	0.47	3.32
	100.00	705.64

Permeate at 30 psia

	%	slpm
CO_2	3.54	21.96
CO	0.03	0.19
CH_4	0.00	0.01
N_2	0.05	0.29
H_2	49.10	304.44
H_2O	25.75	159.69
H_2S	0.00	0.01
N_2 swp	21.53	133.52
	100.00	620.11

Retentate at 691.1 psia

	%	slpm
CO_2	89.87	196.86
CO	2.07	4.54
CH_4	0.22	0.48
N_2	2.96	6.48
H_2	2.21	4.84
H_2O	1.16	2.54
H_2S	1.51	3.31
	100.00	219.05

Membrane parameters:

- H_2 permeance = 80 GPU
- H_2/CO_2 Selectivity = 40
- Dense layer thickness = 1.0 µm
- Membrane area = 8.5 m^2

Operating parameters:

- Feed temperature = 437°F
- 50 kWth Shifted Syngas Feed
- Permeate H_2 recovery = 98.4%
- Retentate CO_2 capture* = 90.0%

* Retentate CO_2 dry basis purity = 96.88% after H_2S removal and catalytic oxidation of CO, H_2 and CH_4

Figure 8: Simulation of a PBI module performance with an oxygen-blown gasifier and a 50-kWth shifted syngas feed.

technology advantages

- PBI combines both useful throughput (permeability) and degree of separation (selectivity).
- PBI is thermally stable up to 300°C and is sulfur tolerant.
- PBI asymmetric hollow fibers can be fabricated at increasingly small diameters, allowing increased fiber packing densities in modules realistically consistent with 7,000 m^2 of membrane surface area per m^3 of module volume.
- Membrane gas separation systems have reduced costs for syngas cooling.
- Membrane gas separation systems should result in reduced CO_2 compression costs.
- Membrane gas separation systems are emissions-free (i.e., they use no solvents such as amines).
- Membrane gas separation systems may have decreased capital costs (assuming membrane costs are managed).
- Membrane gas separation systems have relatively low maintenance demands.
- Membrane gas separation systems are scalable and modular.

R&D challenges

- Maintaining fiber and module fabrication quality/performance (avoiding membrane pinholes, macrovoids, module seal integrity) in scale-up/transfer of technology to larger-scale manufacturing.
- Designing and synthesizing materials structure and configurations.
- Integration and optimization of membrane-based CO_2 separation systems in coal gasification-based plants.

status

Field-testing of the bench-scale skid was started in October 2021 and is continuing through June 2022. The goal is to operate the skid up to 300 hours under the operating conditions and test the performance of the membrane modules with syngas from the gasifier at the host site.

An updated TEA and Technology Maturation Plan (TMP) will be provided after testing concludes in June 2022.

available reports/technical papers/presentations

“Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture.” Presented by Indira Jayaweera and Michael Wales, SRI International, 2021 NETL Carbon Management Research Project Review Meeting. Pittsburgh, PA. August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_0.pdf*

“Development and Testing of a High-temperature PBI Hollow-fiber Membrane Technology for Pre-combustion CO_2 Capture,” presented by Elisabeth Perea, SRI International, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Peria-SRI-High-Temperature-PBI.pdf*

“Development and Testing of a High-temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture,” presented by Indira Jayaweera, SRI International, Final Project Review (FE0012965) and Project Kickoff (FE0031633), January 2019. *https://netl.doe.gov/projects/plp-download.aspx?id=10555&filename=Development+and+Testing+of+a+High-Temperature+PBI+Hollow-Fiber+Membrane+Technology+for+Pre-Combustion+CO2+Capture.pdf*

“Development and Testing of Polybenzimidazole (PBI) Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture (FE0031633),” presented by Indira Jayaweera, SRI International, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/I-Jayaweera-SRI-Hollow-Fiber-Membrane.pdf*

“Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow Fiber Membranes,” presented by Indira S. Jayaweera, SRI International, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2017-12/2I-S-Jayaweera2-SRI-PBI-Hollow-Fiber-Membranes.pdf*

“Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes (HFMs),” presented by Indira S. Jayaweera, SRI International, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/sites/default/files/2017-12/I-Jayaweera-SRI-PBI-Hollow-Fiber-Membranes.pdf*

“Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes,” presented by Indira S. Jayaweera, SRI International, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File Library/Events/2015/co2captureproceedings/I-Jayaweera-SRI-High-Temperature-PBI-HF-Membranes-for-Pre-c.pdf*

“Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane,” presented by Gopala Krishnan, SRI International, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Krishnan-SRI-PBI-Hollow-Fiber-Membranes.pdf*

“Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane Fact Sheet,” July 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0012965.pdf*

“Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes,” Project Kickoff Meeting Presentation, Pittsburgh, PA, June 9, 2014. *https://www.netl.doe.gov/sites/default/files/2017-12/DE-FE0012965-Kickoff-Meeting-June-2014.pdf*

Krishnan, G.; Steele, D.; O’Brien, K.; Callahan, R.; Berchtold, K.; and Figueroa, J., “Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane,” *Energy Procedia*, Volume 1, Issue 1, February 2009, pp. 4079-4088.

Gopala Krishnan; Indira Jayaweera; Angel Sanjurjo; Kevin O'Brien; Richard Callahan; Kathryn Berchtold; Daryl-Lynn Roberts; and Will Johnson,” Fabrication and Scale-up of Polybenzimidazole (PBI) Membrane Based System for Precombustion-Based Capture of Carbon Dioxide,” DOE Contract Number: FC26-07NT43090, 2012-March 31. *http://www.osti.gov/scitech/biblio/1050227*

Bench-Scale Testing of a High-Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture

primary project goal

The main objective is to scale-up and field-validate the technical feasibility of the University of Southern California's (USC) membrane- and adsorption-enhanced water-gas shift (WGS) process that employs a carbon molecular sieve (CMS) membrane reactor (MR), followed by an adsorption reactor (AR), for pre-combustion carbon dioxide (CO_2) capture. The project begins at Technology Readiness Level (TRL) 4, as the system prototype has already been validated in the laboratory on simulated syngas (under predecessor project FE0026423). The project aims to end at TRL 5, via scaling-up of the prototype system and its testing on actual syngas at the University of Kentucky (UKy). Project tasks include designing, constructing, assembling, and validating the bench-scale experimental MR-AR system; preparing suitable membranes, adsorbents, and catalysts needed for the bench-scale system; and deploying the unit at UKy and testing system performance using real syngas. Results are to be used to complete an updated process techno-economic analysis (TEA) and environmental, health, and safety (EH&S) risk assessment.

technical goals

- Demonstrate CO_2 capture from actual coal gasification syngas at a bench-scale syngas flow rate of 50.7 to 253 kg/day, at a temperature of 250°C, at a pressure of 25 atmosphere [atm], and for 500 hours of testing.
- Increase stability of membranes and adsorbents in the process system in terms of degradation by syngas constituents, with an interim target of less than 30% decline in performance over 500 hours of testing at typical syngas conditions.
- Hydrogen (H_2) permeance greater than 1 m^3/m^2.hr.bar for the H_2-selective membrane, with a target range for H_2/carbon monoxide (CO) selectivity exceeding 80.
- Sorbent working capacity greater than 2.5 weight % CO_2; sorbent attrition rate less than 0.2.
- Demonstrate progress (TRL 4 to TRL 5) toward enabling an MR-AR system in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant, capable of CO_2 capture with greater than 95% purity, while reducing the cost of electricity (COE) by 30% over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in an IGCC plant (for shifting the syngas toward primarily H_2 and CO_2) and the downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced in whole by a unique membrane- and adsorption-enhanced WGS reactor system (previously developed for H_2 production via methane steam reforming) that allows for in situ preferential H_2 permeation and

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Hybrid

project focus:
Combined Membrane Reactor and Adsorption Reactor System

participant:
University of Southern California

project number:
FE0031737

predecessor projects:
FE0026423

NETL project manager:
Katharina Daniels
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principal investigator:
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University of Southern California
tsotsis@usc.edu

partners:
Media and Process Technology Inc.; University of California Los Angeles; University of Kentucky Research Foundation

start date:
06.01.2019

percent complete:
92%

simultaneous CO_2 adsorption. The reactor system is depicted, in the context of a typical IGCC power plant cycle, within the blue border-surrounded process block in Figure 1.

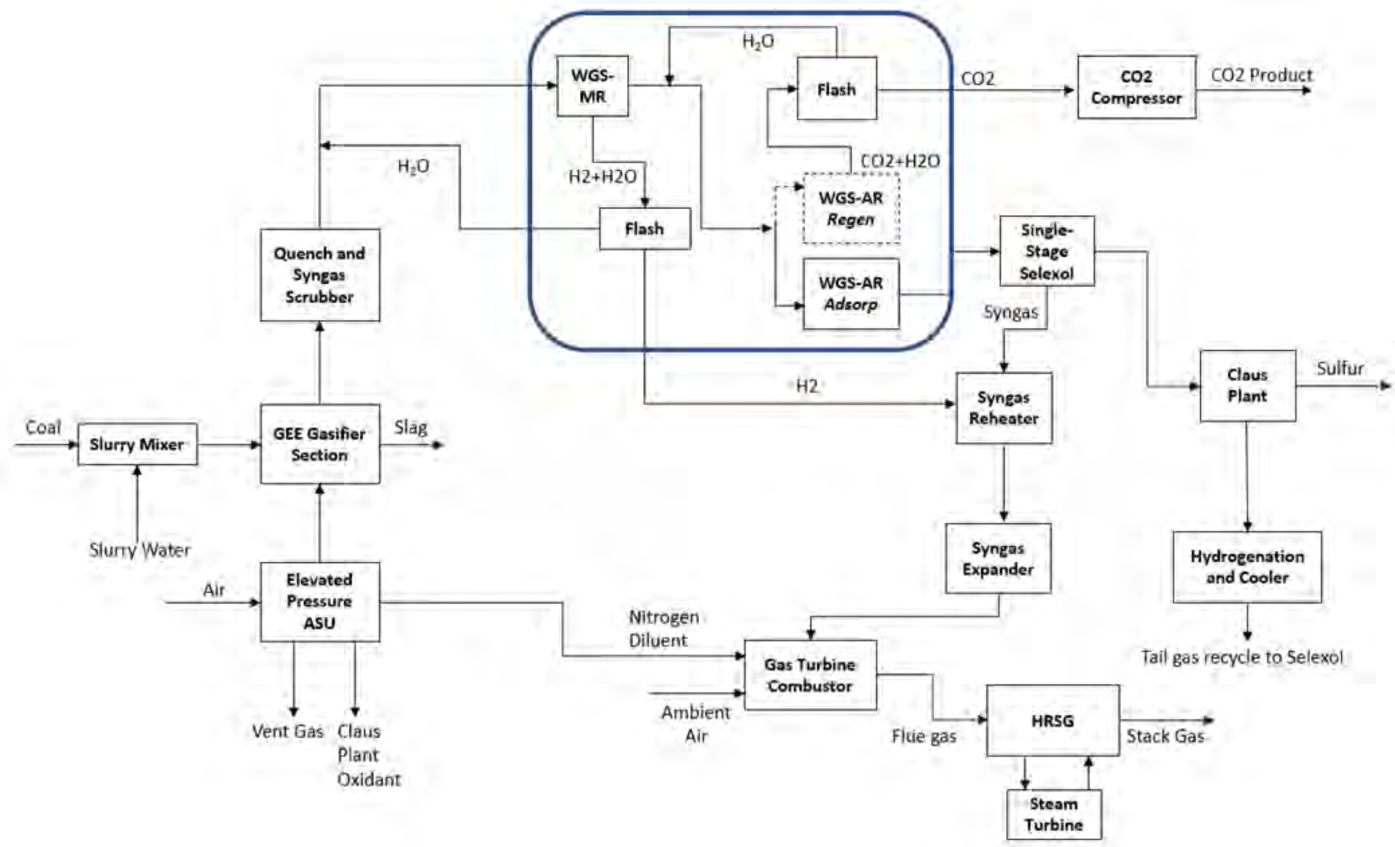

Figure 1: MR and AR system in the context of an IGCC plant process.

The system combines an MR and AR in tandem to continuously produce a pure H_2 product (while attaining greater than 99% CO conversion) until the adsorbent (in the AR unit) is saturated. The AR unit must then be taken off-stream and regenerated via steam-enhanced temperature swing adsorption (TSA). This unique reactor configuration can, therefore, be viewed as a hybrid MR-AR system with TSA cycling. Compared to conventional WGS followed by CO_2 capture using a conventional amine process, the MR-AR system is more efficient and compact. Furthermore, the use of a TSA rather than a pressure-swing CO_2 recovery step (as commonly practiced in AR systems) allows the recovery of CO_2 at higher pressures aiding system efficiency.

The combined MR-AR process is shown in more detail in Figure 2. Here, the syngas first passes into the MR vessel, consisting of WGS catalyst packed around an array of membrane tubes. The tubes are CMS-based membranes on ceramic support, which are highly selective to H_2. The MR permeate consists of high-purity H_2. As the H_2 is withdrawn from the MR vessel, the WGS reaction equilibrium is pushed toward further H_2 production. Retentate/rejected gases are passed to an array of ARs operating in a periodic manner, whereby at any given time some ARs are fed retentate gases and operate in reaction/adsorption mode, while the remaining ARs are fed steam and operate in a TSA regeneration mode. The ARs contain additional WGS catalyst, in addition to CO_2 sorbent. In this technology, hydrotalcite (HTC) is utilized as the CO_2 sorbent. This co-location of the WGS reaction and CO_2 separation functions in the AR allows traditional WGS reaction equilibrium limitations to be overcome, thus enabling enhanced shifting of the syngas to occur until most of the carbon as CO is converted into CO_2 and adsorbed. This results in a relatively pure H_2 gas exiting the AR at high pressure when the ARs operate in reaction/adsorption mode, while a high-pressure steam/CO_2 mixture exits the ARs when they operate in regeneration mode. In summary, the process configuration combining the MR and AR in tandem provides significant process flexibility, efficient high-pressure and high-purity H_2 production, and CO_2 recovery.

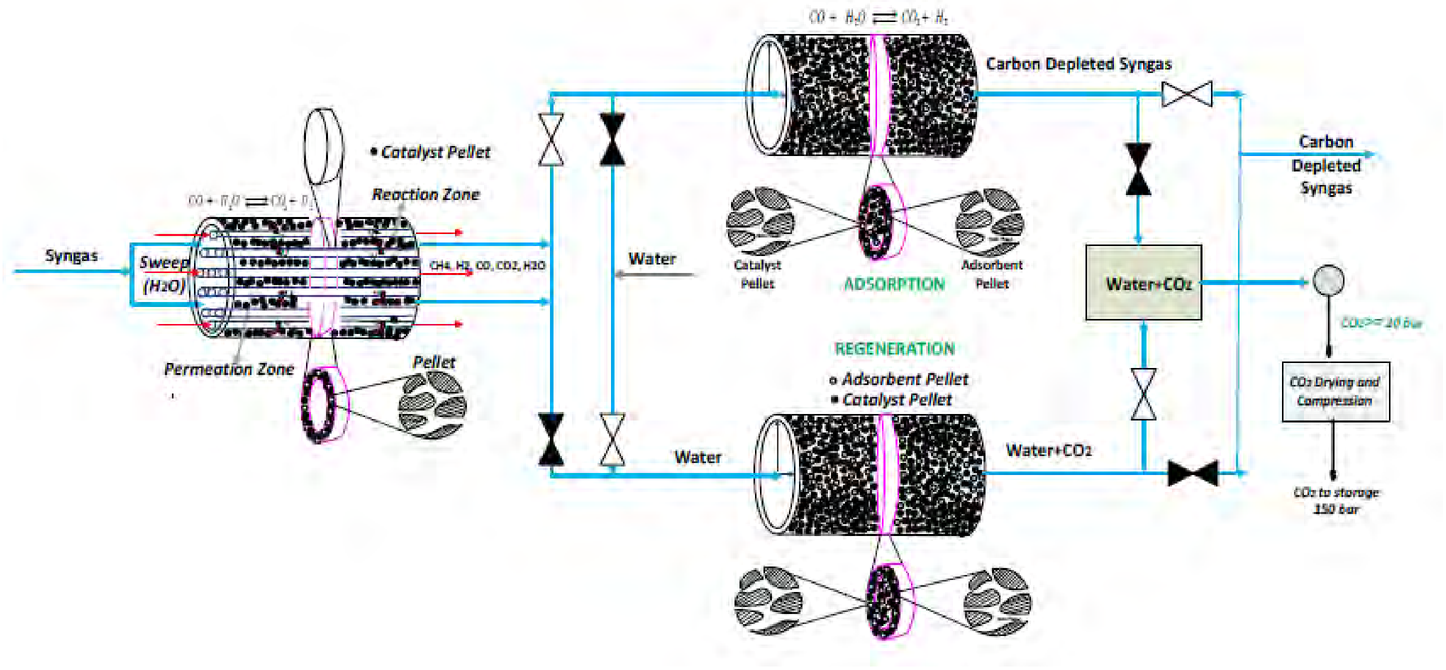

Figure 2: MR-AR process.

The HTC sorbent mentioned previously is an anionic clay magnesium (Mg)/aluminum (Al)-layered double hydroxide, as depicted in Figure 3. It has a relatively high CO_2 capacity over a wide range of temperatures and pressures; can be easily prepared by precipitation of Mg/Al from solution in sodium hydroxide (NaOH); and is unaffected by hydrogen sulfide (H_2S) and simulated tars at anticipated operating temperature, thereby conferring process stability.

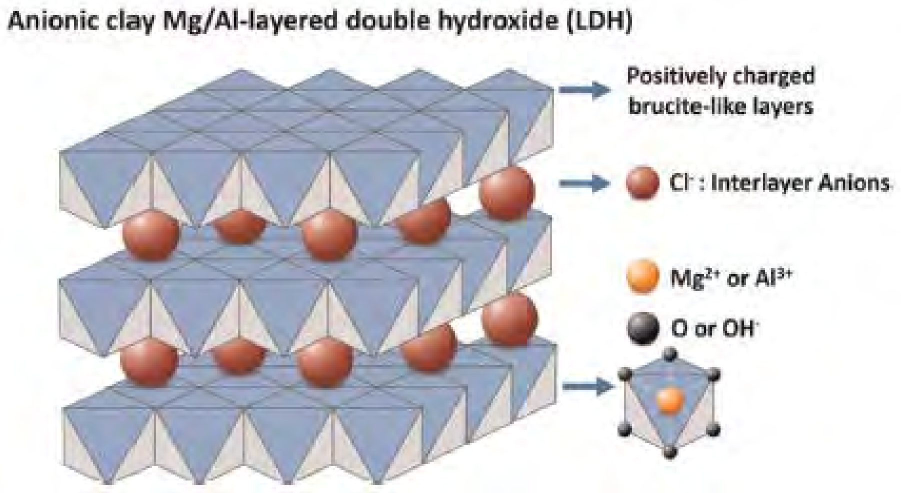

Figure 3: Hydrotalcite (HTC) adsorbent.

The main accomplishments and findings of the USC team's predecessor project included the following:

- CMS membranes were prepared and tested over the full range of expected operating temperatures (up to 300°C) and pressures (10 to 25 bar). Performance targets for H_2 permeance (350 to 550 gas permeation units [GPU]) and H_2/CO selectivity of greater than 80 were met.
- HTC sorbent was prepared, and adsorption/desorption kinetics and working capacity measured at expected operating conditions of 300 to 450°C and pressure up to 25 bar. A performance target for working capacity of greater than 3 weight % CO_2 was met.
- Kinetics of a commercially available sour-shift WGS catalyst were measured at expected operating conditions. This information is essential in modeling and in preparing a TEA of the MR-AR process.

- An MR-AR system operating run of greater than 500 hours was carried out on simulated syngas at a flow rate of less than 0.9 kg/day in a lab-scale integrated experimental apparatus. This effectively advanced the MR-AR technology to TRL 4. Also, the membranes, sorbents, and catalysts were shown to be robust at expected operating conditions.
- Preliminary TEA study results comparing an MR-AR integrated system to a baseline Selexol system (both in the IGCC context) show substantial reductions in required compression work and WGS catalyst requirements. The overall COE target of 30% lower cost than the baseline COE would be closely approached or met given known performance parameters and assumptions.

It should be noted that there are several major points of departure of the case of MR-AR within an IGCC power plant context from the baseline IGCC case. These become important in process performance and cost analysis:

1. The WGS reaction occurs in the MRs and ARs alongside H_2 removal (in the MRs) and CO_2 removal (in the ARs).
2. The amount of steam used in the MR-AR technology serves not only as a reactant but also as a sweep agent to separate the WGS reaction products.
3. A single-stage Selexol unit is needed for H_2S removal, as opposed to a dual-stage Selexol unit for H_2S and CO_2 removal in the baseline case.
4. Steam is used as diluent in the combustion turbine, as opposed to nitrogen (N_2) in the baseline case.

All four of the above items are beneficial from cost, efficiency, and environmental impact viewpoints. The simultaneously reactive-separative nature of the MR-AR units intensifies the kinetic and equilibrium behavior of the WGS reaction, thus resulting in lower catalyst use. It also delivers separate, high-pressure H_2 and CO_2 streams, thus improving process efficiency, economics, and environmental impact through reduced H_2/CO_2 compression costs and reduced Selexol solvent losses/emissions from the single-stage Selexol unit used in MR-AR for H_2S removal compared to the dual-stage Selexol unit used in the baseline. Although, in the MR-AR process, water is used as a WGS reactant, sweeping agent, and H_2 combustion diluent, net water consumption in the MR-AR is only marginally higher than that of the baseline case. This is the result of heat/power/water integration strategies, which additionally result in the availability of N_2 or possible sales that significantly improve process economics, and can also potentially reduce environmental impact, by reducing the possibility of nitrous oxide (NO_X) emissions in H_2 turbine combustion. The use of N_2 as raw material for ammonia (NH_3) production and the current commercialization of NH_3 as an H_2 transport medium greatly enhance the marketability of the MR-AR technology.

Bench-scale testing was sited at UKy's Center for Applied Energy Research (CAER) to enable testing on actual coal-derived syngas from CAER's entrained-flow coal gasifier. The bench-scale unit utilizes 30-inch membrane tubes in 2-inch outer diameter modules for the MR; the process parameters for which are shown in Table 1, while those of the sorbent are shown in Table 2. Test campaigns totaling 500 hours are planned, enabling determination of performance at this larger scale, affording an opportunity to evaluate membrane, catalyst, and sorbent stability over time. The performance data will allow improved TEA of the MR-AR system.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$/m^2	<1,500	<750
Membrane Performance			
Temperature	°C	250–300	250–300
H_2 Pressure Normalized Flux	GPU or equivalent	500	900
H_2/H_2O Selectivity	—	2–4	>3
H_2/CO_2 Selectivity	—	.200	>200
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>10,000	>10,000

Type of Measurement	—	mixed gas		mixed gas
Proposed Module Design				
Flow Arrangement	—		co/counter-current or cross-flow	
Packing Density	m^2/m^3		>450	
Shell-Side Fluid	—		Permeate	
Syngas Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	95	>60
H_2 Recovery, Purity, and Pressure	%/%/bar	>80	>90	Up to 20
Pressure Drops Shell/Tube Side	bar		—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		1,500	

TABLE 2: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value		Target R&D Value
True Density @ STP	kg/m^3	2,849–3,066		2,849–3066
Bulk Density	kg/m^3	1,322–1,423		1,322–1,423
Average Particle Diameter	mm	0.6–0.8		2–3
Particle Void Fraction	m^3/m^3	0.536		0.536
Packing Density	m^3/m^3	0.406		0.406
Solid Heat Capacity @ STP	kJ/kg-K	0.5–0.65		0.5–0.65
Crush Strength	kg_f	N/A		10-15
Manufacturing Cost for Sorbent	$/kg	—		—
Adsorption				
Pressure	bar	25		>25
Temperature	°C	250–300		250–300
Equilibrium Loading	g mol CO_2/kg	~3		~3
Heat of Adsorption	kJ/mol CO_2	~10 kJ/mol		~10 kJ/mol
Desorption				
Pressure	bar	25		>25
Temperature	°C	400–450		<400
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1-0.2		<0.1
Heat of Desorption	kJ/mol CO_2	—		—
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		See Figure 2	
Flue Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90	95	25
Adsorber Pressure Drop	bar		—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

STP – Standard temperature and pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Sorbent Packing Density – Ratio of the active sorbent volume to the bulk sorbent volume.

Sorbent Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figures 1 and 2.

Estimated Cost (Sorbent + Membrane) – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met (see Table 3).

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving.

Contaminant Resistance – Resists all chemical contaminants in gasifier off-gas including H_2S, NH_3, heavy metals, organic vapors, tars, etc., based on bench-scale testing conducted at the National Carbon Capture Center (NCCC).

Syngas Pretreatment Requirements – Particulate removal should be practiced.

Membrane Replacement Requirements – Not known presently but assumed to be five to 10 years. More than 16,000 hours of laboratory thermal stability testing has been demonstrated with no failure. More than 1,000 hours of live syngas testing at NCCC has been conducted with no failure.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Integration – See below.

Entering Module	Pressure	Temperature	Composition						
			vol%						ppmv
	psia.	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
MR	800	440-540	0.1089	0.2823	0.0010	0.0055	0.2689	0.3190	5700
AR	800**	440-540*	0.2480	0.1466	0.0009	0.0055	0.2590	0.3253	5700

* Species compositions shown for inlet temperature of 440°F; **To match the exit gasifier conditions.

TABLE 3: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	9.2—37.4 (Yes-No N_2 sold) 63.2 (B5B Baseline)	N/A
Cost of Carbon Avoided	\$/tonne CO_2	23.1—66.4 (Yes-No N_2 sold) 91.7 (B5B Baseline)	N/A
Capital Expenditures	\$/MWhr	56.9—60.4 (No-Yes N_2 sold) 74.2 (B5B Baseline)	N/A
Operating Expenditures	\$/MWhr	26.3—28.0 (No-Yes N_2 sold) 30.4 (B5B Baseline)	N/A
Cost of Electricity	\$/MWhr	89.1—109.8 (Yes-No N_2 sold) 135.4 (B5B Baseline)	94.8

technology advantages

- Improved WGS efficiency: hybrid concept process allows the simultaneous removal from the reacting phase and recovery of both H_2 and CO_2, resulting in significant reaction rate enhancement over the conventional WGS system.
- Significantly reduced catalyst weight usage requirements: reaction rate enhancement (over conventional WGS) permits operation at lower weight of catalyst/inlet molar flow rate of CO (W/F_{CO}), thus resulting in significant catalyst savings.
- No syngas pretreatment required given use of sour-shift catalyst and use of CMS membranes, which have demonstrated stability to all gaseous contaminants present in coal-derived syngas.
- Efficient H_2 production and superior CO_2 recovery and purity: the synergy of the MR and AR units satisfies the CO_2 recovery/purity, carbon utilization (CO conversion), and H_2 recovery/purity goals.

R&D challenges

- Heat management in reactors.
- Process integration with IGCC.
- Particulate matter needs to be controlled to reduce its potential impact on the reactor units.
- Scale-up and integration issues, given the large number of reactor modules needed to service a 550-MWe plant.

status

Design and construction of the bench-scale unit for testing at UKy CAER has been completed. All utility connections have also been completed, and testing is currently underway. Schematics, photographs, and system description were provided in quarterly reports.

available reports/technical papers/presentations

"Bench-Scale Testing of a High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture," presentation by Theo Tsotsis, University of Southern California, 2020. Budget Period 1 Report Meeting. November 2020.

"*A High Efficiency, Ultra-compact Process for Pre-combustion CO_2 Capture*," presentation by Theo Tsotsis, University of Southern California, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/T-Tsotsis-USC-Ultracompact-Capture.pdf*.

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Alkanolamines for Acid Gas Removal in Gasification Processes

primary project goal

Pacific Northwest National Laboratory (PNNL) performed this project to identify and evaluate advanced carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) solvents suitable for pre-combustion removal of CO_2 from syngas. Such solvents would outperform baseline/standard solvents (e.g., Selexol) in terms of improved CO_2 uptake capacity, low viscosity, and excellent gas selectivities, and might serve as a drop-in replacement in a conventional amine-based capture process.

technical goals

- Collect critical experimental data and complete a techno-economic assessment (TEA) for greater than 90% CO_2 removal with an energy penalty for the CO_2 capture of less than 0.7 GJ/tonne for pre-combustion capture with CO_2BOL solvents.
- Optimize PNNL's blended pressure swing absorption (PSA) and thermal swing absorption (TSA) solvent formulations to obtain the best CO_2 uptake capacity, low viscosity, excellent carbon monoxide (CO) and hydrogen (H_2) selectivities while removing more than 98% CO_2.
- Make progress toward meeting the U.S. Department of Energy's (DOE) overall performance goals of CO_2 capture with 95% CO_2 purity at a cost of electricity (COE) 30% less than baseline capture approaches.

technical content

To begin this effort, PNNL performed screening for CO_2BOL solvents suitable for removal of CO_2 from syngas. Three alkanolamine PSA solvents were selected for screening: N-ethyldiethanolamine (EDEA), dimethylaminoethanol (DMEA) (see Figure 1 top), and a proprietary solvent formulation that PNNL designates as DEEEA. Additionally, four TSA regeneration solvents were evaluated for this application: three aminopyridines including 2-[(methylamino)methyl]pyridine (2-MAMP), 2-[(ethylamino)methyl]pyridine (2-EAMP) (see Figure 1 bottom), and a proprietary aminopyridine designated AP, plus the diamine N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA). EDEA and DMEA solvents have shown promising CO_2 uptake capacity with both chemical and physical absorption, but the performance dropped significantly in mixed gases. The aminopyridines (2-MAMP, 2-EAMP, and AP) and EEMPA bind CO_2 chemically at ambient pressure with potential additional physical absorption under elevated pressures.

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-combustion Power Generation PSC

key technology:
Solvents

project focus:
CO_2-Binding Organic Liquid Solvents for Pre-Combustion CO_2 Capture

participant:
Pacific Northwest National Laboratory

project number:
FWP-72564

predecessor projects:
N/A

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partners:
Susteon Inc.

start date:
10.01.2018

percent complete:
100%

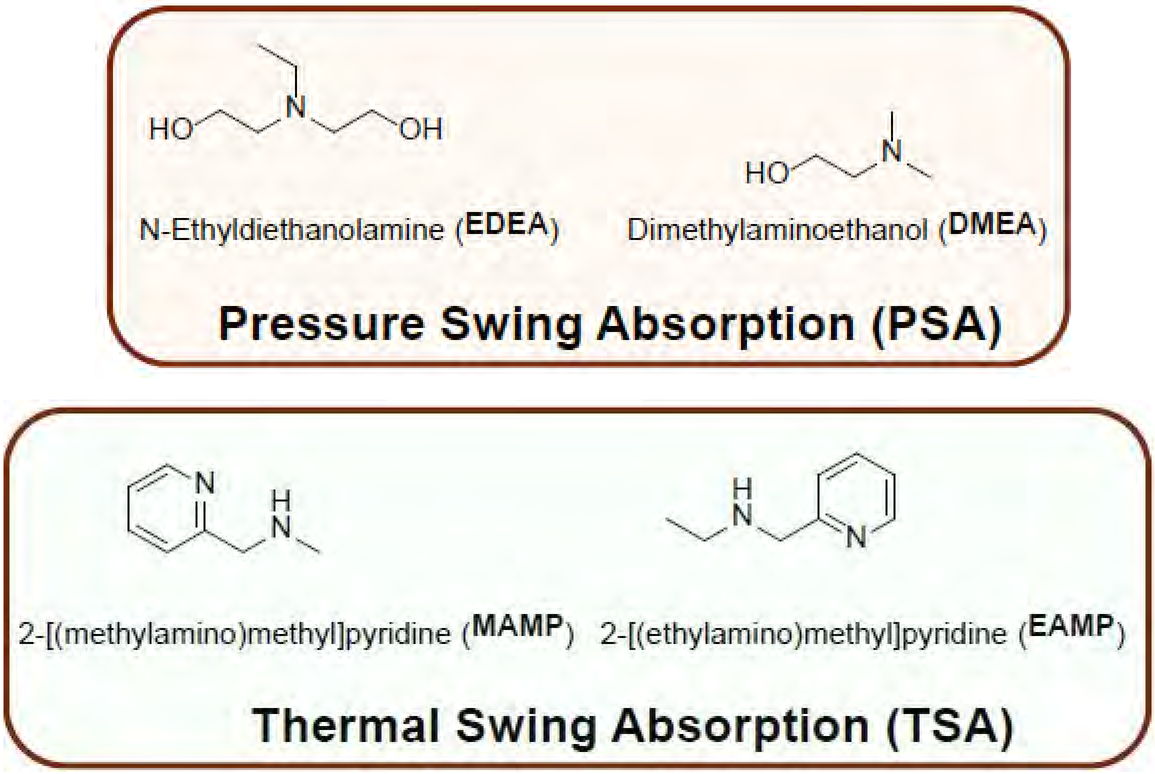


Figure 1: Certain non-proprietary amine solvents tested for CO_2 capture.

In order to improve the CO_2 solubility of PSA solvents such as EDEA and DMEA, the new solvent DEEEA was designed using learnings from past post-combustion CO_2 capture work to increase CO_2 solubility while lowering viscosity. VLE measurements for DEEEA solvent showed the highest physical solubility (42.22 mol% of CO_2) compared to all CO_2BOL solvents. It also showed minimal chemical absorption of 1.38 mol% as carbonate, resulting into a total uptake capacity 43.6 mol%. DEEEA exhibited similar drop in CO_2 capacity in mixed gases as EDEA and DMEA.

TSA solvents EEMPA and AP exhibited excellent CO_2 uptake capacity without significant drop in mixed gases, but they suffered from increased viscosity under syngas conditions. It was hypothesized that a blend of the best thermal- and pressure-swing solvents would result in a formulation with high CO_2 capture capacity and low viscosity. To evaluate this concept, controlled blends of EEMPA (the best thermal swing solvent) and DEEEA (the best pressure swing solvent) were made, and the VLE data of these blends were measured. The gravimetric CO_2 uptake capacity of the DEEEA:EEMPA blends shows a good uptake capacity under both pure CO_2 and mixed gas containing CO_2 and H_2. These solvent formulations have negligible H_2 uptake under gravimetric conditions.

A blend of the 1:1 mole ratio of EEMPA and DEEEA was selected for VLE studies using a redesigned high-pressure NMR cell. Figure 2 shows VLE data for 1:1 DEEEA:EEMPA for CO_2:H_2 (1:1) gas mixture at 35 bar. This figure shows high CO_2 uptake and VLE as a function of temperature follows the expected trend of decreasing uptake with increased temperature.

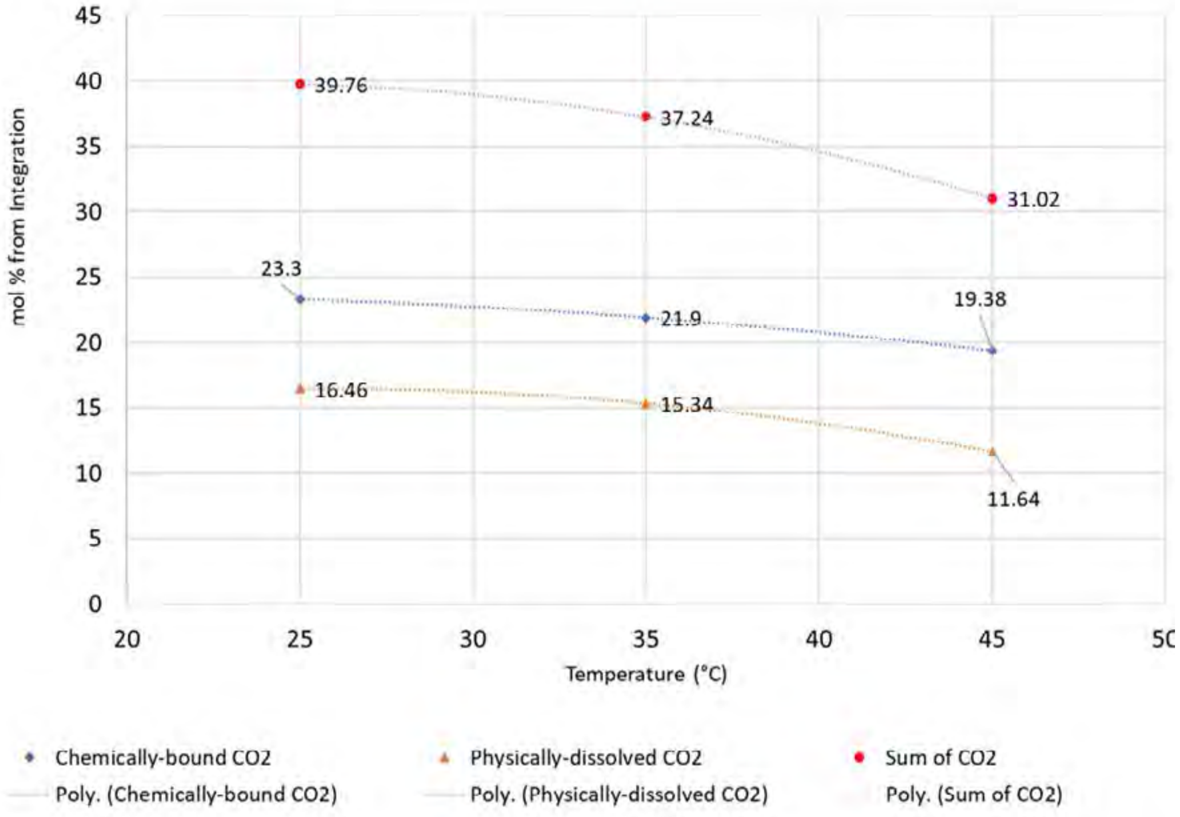


Figure 2: VLE for 50:50 DEEEA:EEMPA for CO_2:H_2 (1:1) gas mixture at 35 bar.

Low viscosity of the CO_2-rich solvent is critical for both low capital and operation cost of the process. To understand the viscosity of the promising formulation, the viscosity was measured at a CO_2 pressure of 500 pounds per square inch (psi). Figure 3 shows the viscosity of DEEEA:EEMPA for three different proportions (10:90, 30:70, and 80:20) as a function of temperature. Viscosity is lower for blends with more DEEEA, with viscosity of the 10:90 blend preferred as the viscosity measured is similar to that of baseline aMDEA solvent.

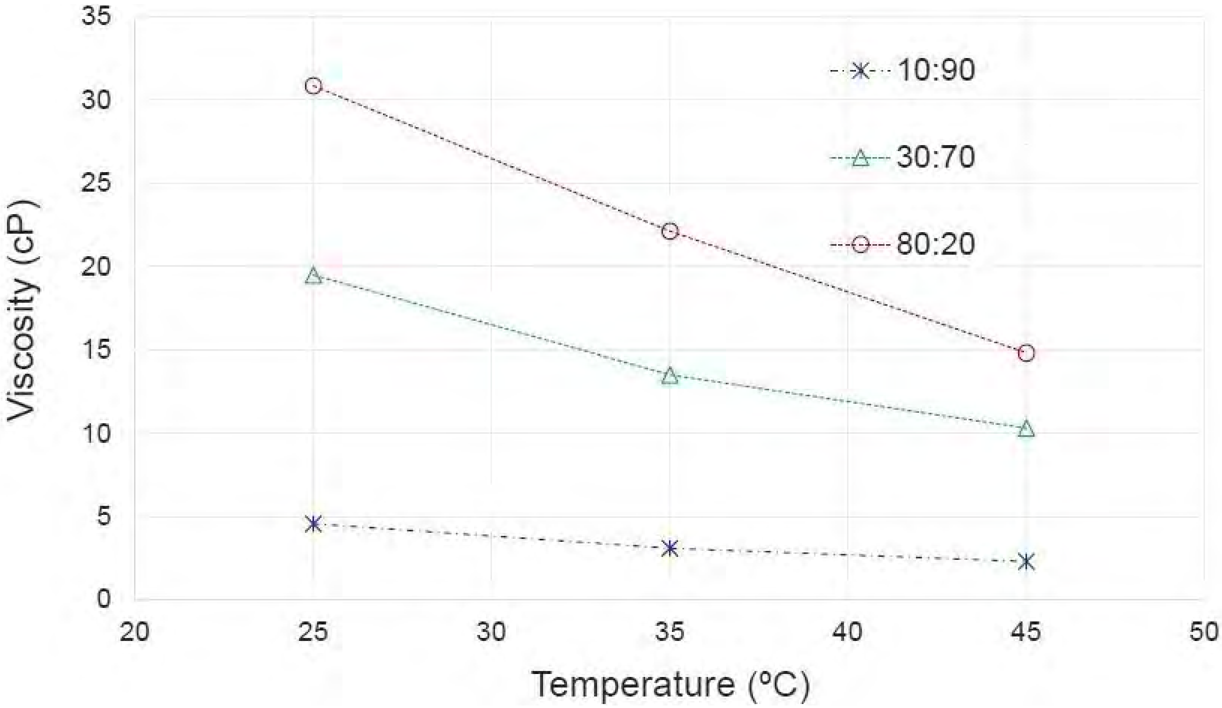


Figure 3: Viscosity versus temperature of DEEEA:EEMPA blends under 500 psi CO_2.

PNNL needed alternative methods to NMR for measuring high-pressure VLE, viscosity, density, and vapor pressure of these solvent mixtures. For this purpose, they designed, constructed, and validated a testing cell system utilizing gas chromatograph-mass spectrometer evaluation of gas phase sampling; simultaneous absorption rate and mass transfer evaluations, along with VLE on solvent samples using an internal Wetted Wall Contactor (WWC); and simultaneous viscosity measurement on CO_2 loaded samples, expandable to other physical properties (e.g., density). After successful validation with solvents aMDEA and propylene carbonate, for which ample experimental data are available, the system was used to determine VLE for DEEEA:EEMPA (90:10) as depicted in Figure 4, with the intent that this solvent blend would be assumed in process simulations supporting a TEA of a pre-combustion capture system per process performance determination featured as a project technical objective.

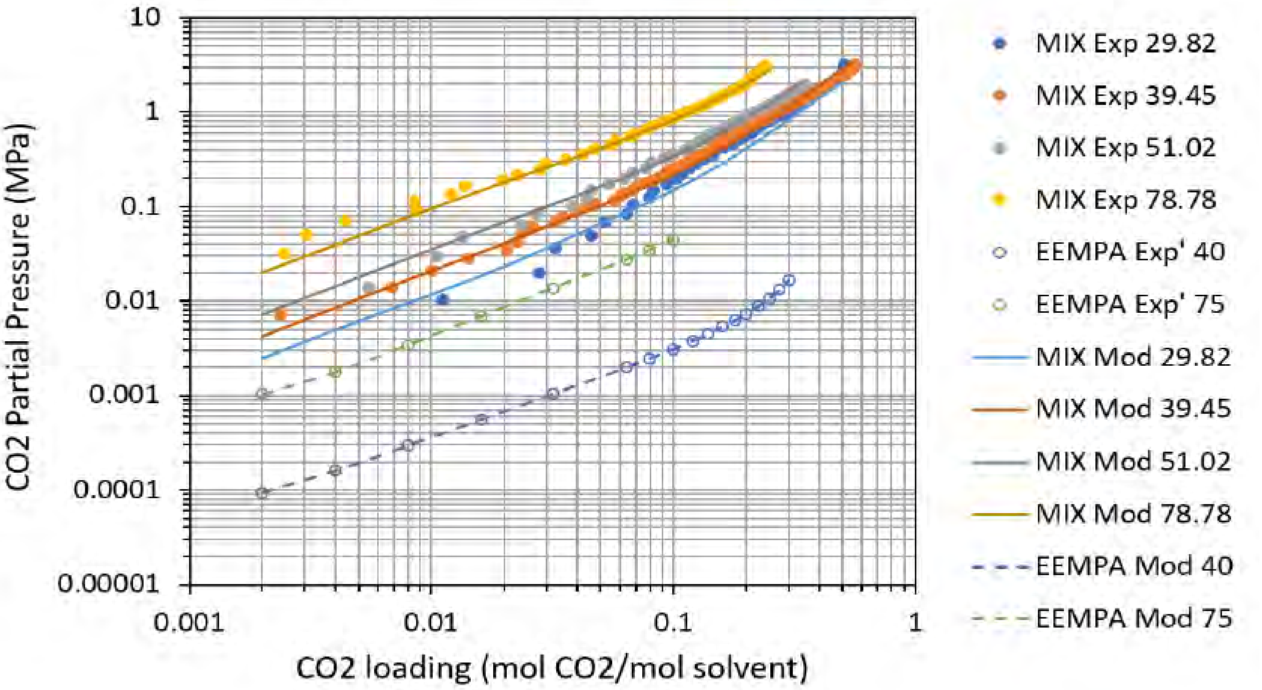
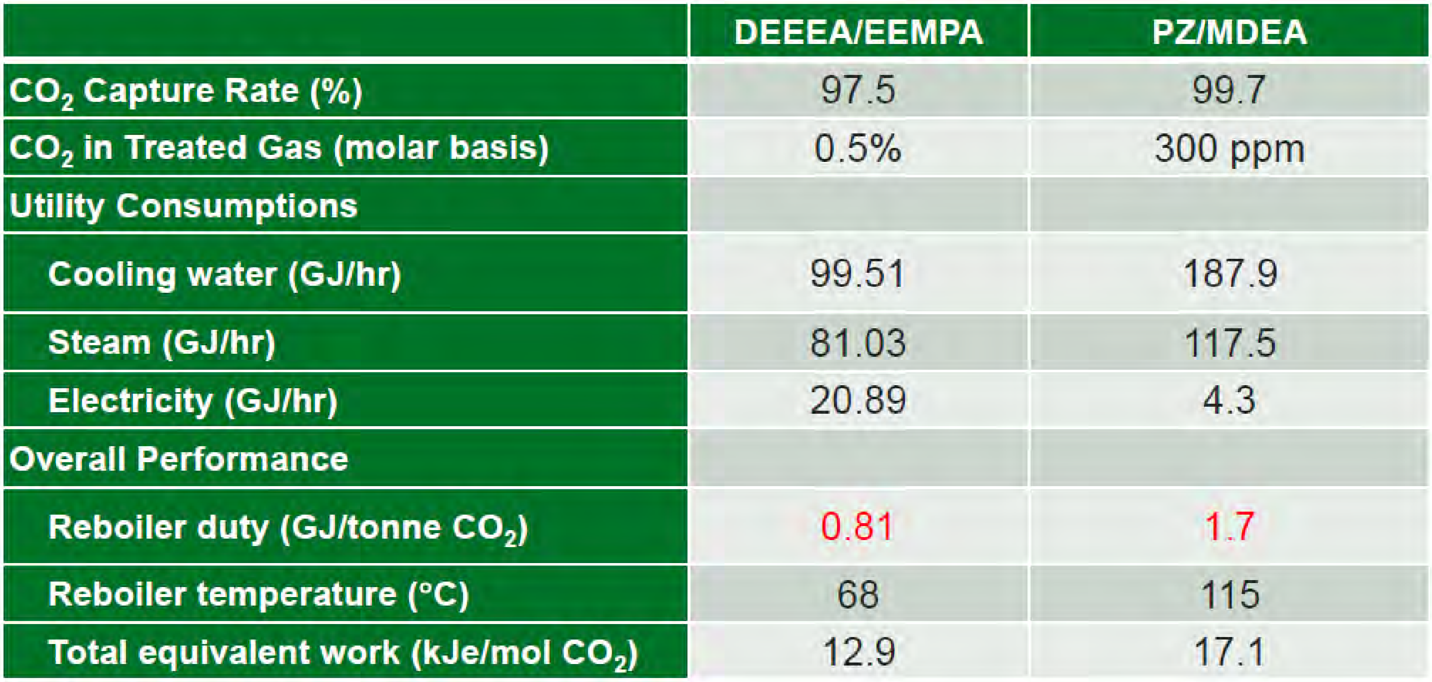


Figure 4: VLE for DEEEA: EEMPA (90:10).

Equilibrium CO_2 partial pressure VLE curves for 90:10 DEEEA:EEMPA at approximately 30, 40, 50, and 80°C show expected trend of decreasing CO_2 uptake capacity with increased temperature. ASPEN Plus simulation of the VLE curves match experimental data with minor deviation at higher CO_2 loading. Also, simulation of the viscosities agrees with experimental data, with the highest solvent viscosity in the presence of CO_2 at around approximately 3 cP, which is acceptable for industrial application.

With solvent properties validated by experimental data, partner Susteon developed a series of process configurations to maximize the CO_2 capture efficiency of the solvent, while minimizing the overall energy requirement and capital cost of the process. This analysis prompted a regeneration scheme with a combination of a flash pressure-reduction and a small reboiler. Results from this analysis indicated that DEEEA/EEMPA solvent can remove 97.5% CO_2 with reboiler heat consumption of 0.81 GJ/tonne CO_2, which is 47% lower than that of aMDEA for an unoptimized process. Overall, comparing the DEEEA/EEMPA solvent to conventional amine solvents, these values (as summarized in Figure 5) show that there is a strong potential to achieve up to a 25% improvement in the total energy for CO_2 capture from high-pressure syngas mixtures using the new mixed solvent as a replacement for drop-in solvent in existing commercial aMDEA plants.

According to these findings, a drawback remains—90:10 DEEEA:EEMPA does not achieve the industry target of greater than 99.7% capture rate and 300 parts per million (ppm) (molar basis) CO_2 in treated gas. As such, optimization of the DEEEA/EEMPA formulation needs further attention in future work.



	DEEEA/EEMPA	PZ/MDEA
CO_2 Capture Rate (%)	97.5	99.7
CO_2 in Treated Gas (molar basis)	0.5%	300 ppm
Utility Consumptions		
Cooling water (GJ/hr)	99.51	187.9
Steam (GJ/hr)	81.03	117.5
Electricity (GJ/hr)	20.89	4.3
Overall Performance		
Reboiler duty (GJ/tonne CO_2)	0.81	1.7
Reboiler temperature (°C)	68	115
Total equivalent work (kJe/mol CO_2)	12.9	17.1

Figure 5: Process performance comparison.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	206.4	206.4
Normal Boiling Point	°C	TBD	—
Normal Freezing Point	°C	TBD	—
Vapor Pressure @ 15°C	bar	TBD	—
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.99	—
Specific Gravity (20°C/20°C)	-	0.964	—
Specific Heat Capacity @ STP	kJ/kg-K	1.6	—
Viscosity @ 15°C	cP	~2	~5
Absorption			
Pressure	bar	35	35
Temperature	°C	35-48	25-45
Equilibrium CO_2 Loading	mol/mol	0.10	—
Heat of Absorption	kJ/mol CO_2	35	—
Solution Viscosity	cP	2	—
Desorption			
Pressure	bar	1.3	1.3
Temperature	°C	44/68*	68
Equilibrium CO_2 Loading	mol/mol	0.02	—
Heat of Desorption	kJ/mol CO_2	35	—
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	97.5 99.7 35	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*Two-stage desorption is used

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Combination of physical and chemical.

Solvent Contaminant Resistance – Currently unknown.

Solvent Foaming Tendency – Currently unknown.

Flue Gas Pretreatment Requirements – Currently unknown.

Solvent Makeup Requirements – Currently unknown.

Waste Streams Generated – Currently unknown.

Process Design Concept – The DEEEA/EEMPA mixed solvent can be used as a drop-in replacement solvent in a commercial aMDEA CO_2 capture process, as depicted in Figure 6.

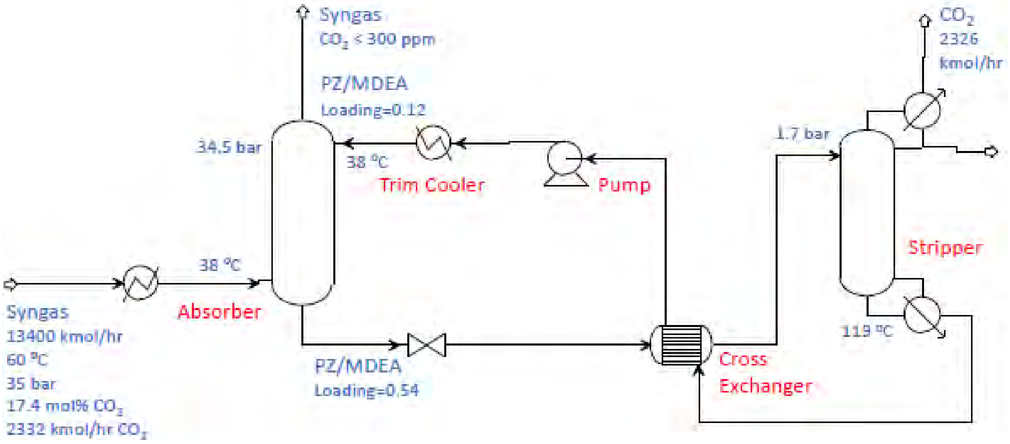


Figure 6: Configuration and operating conditions of the aMDEA process.

technology advantages

- Low regeneration energy requirements (less than 0.7 GJ/tonne CO_2).
- Lower capital cost from small equipment resulting from higher CO_2 capacity and CO_2 selectivity.
- Mixed DEEEA:EEMPA solvent can be used as a drop-in replacement in an aMDEA process.

R&D challenges

- Resource risks, including availability of equipment and staff availability.
- Effect of flue gas contaminants is currently unknown.
- Improving performance in mixed gases versus pure CO_2.

status

The project was completed at the end of March 2021.

A new PSA solvent was developed, DEEEA, which was designed to improve CO_2 solubility without increasing viscosity. This new solvent had the highest physically absorbed CO_2 of all CO_2BOLs (about 44 mol%), but similar to the other PSA solvents, the CO_2 uptake capacity significantly dropped in mixed gases. Thus, it is not able to achieve greater than 90% CO_2 capture from syngas streams.

The TSA solvents, namely 2-MAMP, 2-EAMP, EEMPA, and AP, had high-gravimetric CO_2 uptake capacity, but were disadvantaged by high viscosity.

It was found that VLE for blends of EEMPA and DEEEA showed the best CO_2 uptake with a combination of both chemical and physical absorption of CO_2 without significant drop-in uptake in binary and ternary gas mixtures.

Process simulation results showed that the mixed solvent (DEEEA:EEMPA) process uses lower overall energy, with strong potential to achieve up to a 25% improvement in the total energy for CO_2 capture from high-pressure syngas mixtures using the new mixed solvent as a replacement for drop-in solvent in existing commercial aMDEA plants. However, a drawback remains in that the industry target of greater than 99.7% capture rate and 300 ppm (molar basis) CO_2 in treated gas is not quite met. As such, optimization of the DEEEA:EEMPA formulation needs further attention in future work.

available reports/technical papers/presentations

“Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration,” Final Project Meeting Presentation for Project Number FWP-72564, Phillip Koech & David Heldebrant, March 24, 2021.

Koech, P. “Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration,” NETL Carbon Capture 2020 integrated Review Webinar, October 5–7 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Koech.pdf*.

Koech, P. “Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration,” NETL Carbon Capture Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Koech-PNNL-Syngas%20Purification.pdf*.

Integrated Multichannel Water-Gas Shift Catalytic Membrane Reactor for Pre-Combustion Carbon Capture

primary project goal

The Bettergy Corporation team has been developing an integrated catalytic membrane reactor (CMR) system that combines, in a one-stage process, a high-temperature water-gas shift (WGS) reaction with a hydrogen (H_2) separation membrane to produce H_2 while simultaneously delivering carbon dioxide (CO_2) at high pressure, minimizing the cost of CO_2 compression. The novel process depends on a robust modularized membrane supported on catalytic substrates, which is based on Bettergy's patented nanopore engineering membrane platform technology. Previously, a lab-scale WGS-CMR system was successfully tested, achieving high WGS conversion, high-purity H_2 through membrane separation, and enriched CO_2 in the retentate stream. Currently, the main project goals are to optimize the process, develop and test a multichannel prototype system, and generate a commercialization plan.

technical goals

- Optimize the formulation for the catalytic membrane substrate.
- Develop and optimize the fabrication processes for making both tubular and multichannel membrane substrates.
- Optimize membrane synthesis procedures on the substrates.
- Optimize CMR performance to attain carbon monoxide (CO) conversion exceeding the thermodynamic limit at high temperature (up to 500°C) and pressure of 450 pounds per square inch (psi).
- Investigate the effect of impurities (e.g., hydrogen sulfide [H_2S]) on membrane performance, and achieve stability of at least 500 hours without appreciable degradation.
- Demonstrate prototype performance at syngas (simulated) flow rate of 5 kg/day.
- Enable improvement of energy efficiency of a WGS-CMR system integrated in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant with CO_2 capture by 25 to 30%, relative to a multistage WGS reaction with amine-based carbon capture and pressure swing adsorption (PSA) H_2 purification.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification or steam reforming plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit (for capturing the CO_2 from the shifted syngas) could be replaced in whole by a one-stage WGS-CMR process unit. In this one-stage process, the WGS reaction occurs in the CMR, which incorporates H_2 separation membranes that permit pure H_2 to be drawn off, efficiently increasing the driving force for the equilibrium WGS reaction to go to completion. Carbon dioxide exiting the WGS-CMR

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Water-Gas Shift Catalytic Membrane Reactor

participant:
Bettergy Corporation

project number:
SC0018853

predecessor projects:
N/A

NETL project manager:
David Lang
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principal investigator:
Zhong Tang
Bettergy Corporation
ztang@bettergy.com

partners:
University of Cincinnati;
Dawnbreaker Inc.

start date:
07.02.2018

percent complete:
85%

remains at relatively high pressure, reducing subsequent CO_2 compression costs. As a result, the multiple stages of the conventional WGS unit would be replaced by a single-stage reactor (or banks of reactors in parallel as syngas throughput requires). The process concept is depicted in Figure 1 (for a natural gas reforming scenario).

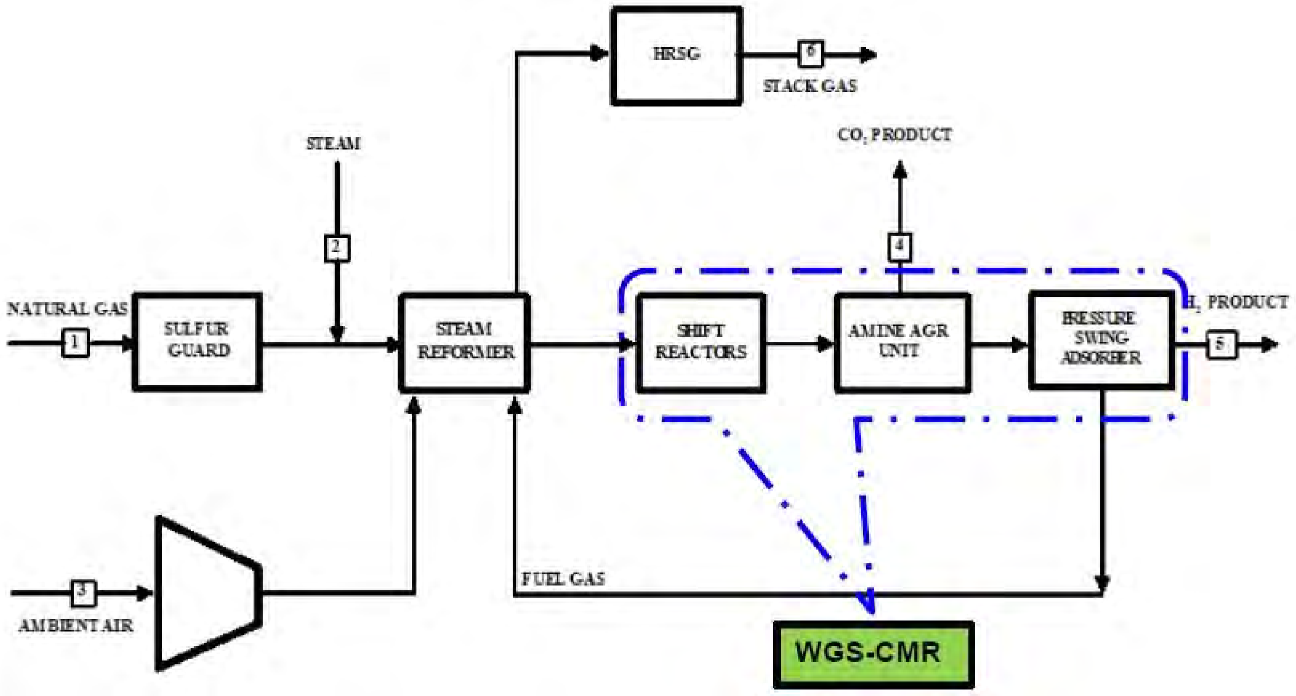


Figure 1: WGS-CMR (in green shadow) replacing two-stage shift, amine CO_2 capture, and PSA systems (in blue envelope) in natural gas steam reforming H_2 production process.

The basic structure of the WGS-CMR consists of tubular channels having a configuration of the sort illustrated in Figure 2. Each reactor gas channel consists of a porous tubular support on which two different active layers are applied. The internal tube layer is made of WGS catalyst, while the outer layer is an H_2-selective zeolite. Pressurized syngas flows through the bores of the tubes, where it contacts the WGS catalyst layer inducing increased H_2 production. The H_2 permeates through the support and can exit through the outside selective layer. Other syngas species do not readily permeate through the outside zeolite layer and remain at pressure inside the tubes. Given suitable WGS kinetics and gas flow rates, high levels of syngas conversion can be obtained, and a large fraction of H_2 can be recovered on the permeate side of the reactor. Retentate from the reactor can be made to contain most of the carbon in the incoming syngas in the form of CO_2. An alternate WGS-CMR configuration is similar but dispenses with the WGS layer and has only an H_2-selective layer on a porous substrate of WGS catalyst. In this case, the WGS catalyst may be in monolith form with many channels, with the H_2-selective zeolite layer on the outside surface of the monolith.

The dimensions of the gas channels may be made very small, and as such the WGS-CMR is a type of microchannel membrane reactor. Microchannel reactors offer multiple benefits, including better control over temperature profiles, minimal catalyst loading for given levels of gas throughput, moderate pressure drop, and favorable trade-off between capital cost and performance.

This novel WGS-CMR does pose developmental challenges, including optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate), preparing the H_2-selective composite zeolite thin layer membrane on the support/substrate, and development and optimization of WGS-CMR assemblies.

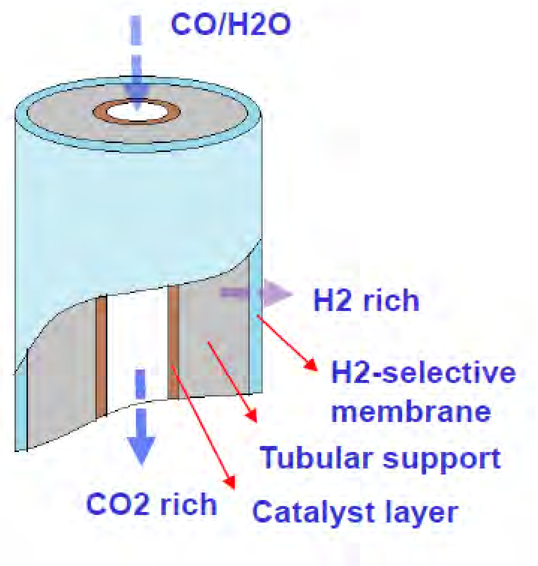


Figure 2: WGS-CMR tubular configuration.

One closely investigated configuration is a catalytic tubular substrate (CTS), which consists of WGS catalyst incorporated into the tubular support itself. A mixture of alumina and WGS catalyst powder (FeCr), plus binders/additives, has been extruded in single-channel tubes and sintered/heat treated (see Figure 3). This process has been optimized, resulting in CTSs with 1-inch diameter reliably prepared and reaching a length of 30 cm free of cracks. These include a surface modification technique for zeolite seed layer coating and membrane in situ growth.

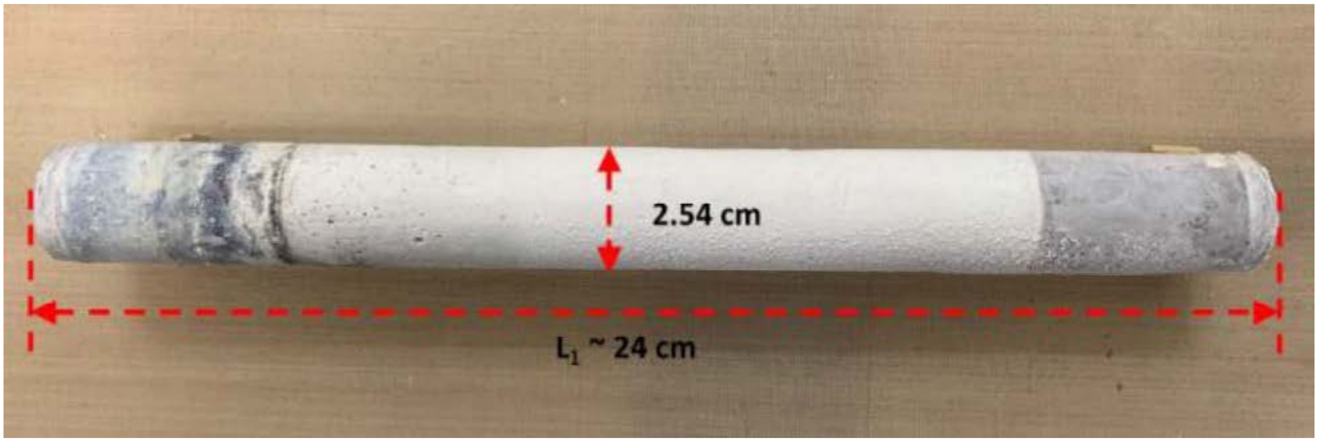


Figure 3: Post-heat-treated catalytic tube substrate.

To achieve high permeance of hydrogen, the hydrogen-selective layer on the substrate must be as thin as possible. The Bettergy team has been developing what is termed a zeolite nanosheet laminated membrane (ZNLM); they have succeeded in synthesizing a silicalite ZNLM on catalyst-alumina composite disc supports (Si-ZNLM-Cat) with minimized defects as indicated by favorable H_2/CO_2 separation selectivity of less than 0.5; also, the Si-ZNLM-Cat demonstrated enhanced CO conversion when operated as a membrane reactor for the WGS reaction at 500°C and 10 bar reaction pressure. The results indicate that ZNLM-Cat can be fabricated with reasonably well-preserved catalytic activity and membrane integrity for high-temperature WGS in a membrane reactor configuration. Figure 4 shows scanning electron microscopy (SEM) image of the Si-ZNLM on the catalytic disc support. Although the membrane surface appears to be covered by discrete zeolite particles, the Si-ZNLM is dense and continuous underneath, with uniform thickness of the membrane about 2.5 µm.

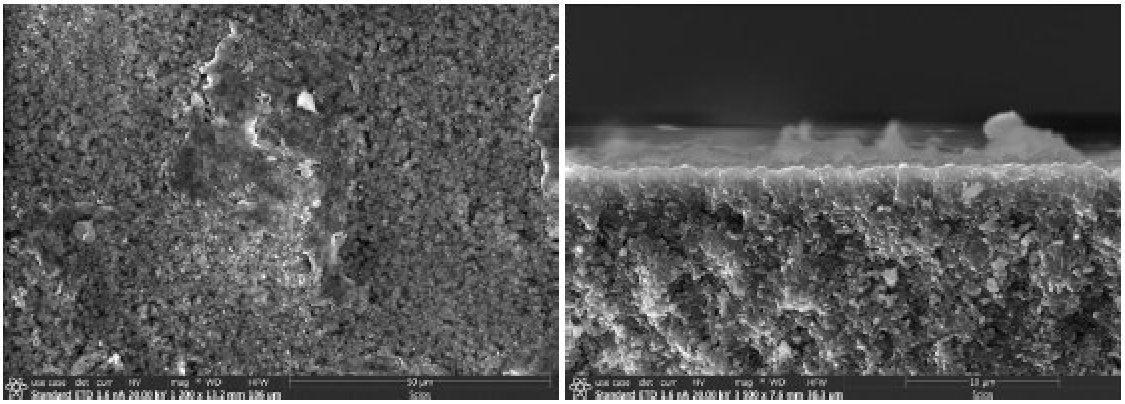


Figure 4: SEM images of the Si-ZNLM membrane: (left) surface and (right) cross-section.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	composite	composite
Materials of Fabrication for Support Layer	—	WGS catalyst	WGS catalyst
Nominal Thickness of Selective Layer	µm	10-20	10-20
Membrane Geometry	—	tubular	multichannel
Max Trans-Membrane Pressure	bar	10-30	30
Hours Tested without Significant Degradation	—	500	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	1,000	355-657
Membrane Performance			
Temperature	°C	350-550	400-500
H_2 Pressure Normalized Flux	GPU or equivalent	150	50-250
H_2/H_2O Selectivity	—	N/A	N/A
H_2/CO_2 Selectivity (Dense layer thickness)	—	>50	>75
H_2/H_2S Selectivity (Dense layer thickness)	—	N/A	N/A
Sulfur Tolerance	ppm	200	500
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	counter flow	
Packing Density	m^2/m^3	n/a	
Shell-Side Fluid	—	retentate	
Syngas Flowrate	kg/hr	0.21	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80%, 80%, 20 bar	
H_2 Recovery, Purity, and Pressure	%/%/bar	80%, >95%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	1/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	0.12	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, monolith, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – TBD.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – Hydrogen sulfide would remain in the retentate and must be separated. This may result in a waste stream containing H_2S.

Process Design Concept – See Figure 1.

Proposed Module Integration – TBD.

The composition of the gas entering the module:

Pressure	Temperature	Composition (Dry)						
psia	°F	vol%						
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435.1	842	15.95	49.75	0.12	1.15	32.55	0.46	0.02

technology advantages

- The novel pre-combustion CO_2 capture technology can be used in current gasification plants or future IGCC plants for industrial H_2 production while simultaneously capturing CO_2.
- Bettergy's CMR system offers substantial simplification of the CO_2 capture process, reduction in the cost of CO_2 capture, and increased energy efficiency, providing economic and environmental benefits for the general public.
- Microchannel reactors facilitate favorable operating temperature profiles in the reactor.
- Microchannel reactors minimize catalyst loading and limit pressure drop.
- Microchannel reactors provide optimized balance between capital cost and performance.

R&D challenges

- Optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate).
- Preparation of the H_2-selective composite zeolite thin layer membrane on the support/substrate.
- Development and optimization of WGS-CMR assemblies.
- "Trade-off" of membrane separation factor and catalyst activity, as governed by catalytic reaction intrinsic kinetics, gas diffusion mechanisms in the catalyst/membrane, and membrane properties.
- Fabrication of high-quality multi-channel catalytic substrates due to lack of satisfactory commercially available extruding machines.

status

Fabrication methods for single-channel and multi-channel tubular catalytic substrates have been developed, and successful formation of zeolite membrane layer on catalytic surfaces has been accomplished. Evaluation of performance has shown increased CO conversion via the WGS-CMR concept.

available reports/technical papers/presentations

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I final briefing/Phase II kickoff meeting, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12097&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-Combustion+Carbon+Capture.pdf*

"Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture," Phase I kickoff meeting presentation, July 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12098&filename=Integrated+Multichannel+WGS+Catalytic+Membrane+Reactor+for+Pre-combustion+Carbon+Capture.pdf*

US Provisional Patent Application No. 63/150,253, "Integrated multichannel membrane reactor," 2021.

High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Ceramic-Carbonate Dual-Phase Membrane Reactor for CO_2 Capture from Coal Syngas

participant:
Arizona State University

project number:
FE0031634

predecessor projects:
N/A

NETL project manager:
Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:
Jerry Lin
Arizona State University
jerry.lin@asu.edu

partners:
University of South Carolina

start date:
10.01.2018

percent complete:
90%

primary project goal

Arizona State University (ASU), in collaboration with the University of South Carolina (USC), are developing technology for a high-temperature, high-pressure, ceramic-carbonate dual-phase (CCDP) membrane reactor. The reactor is intended to perform the water-gas shift (WGS) reaction on syngas (maximizing hydrogen [H_2] content of the syngas) while simultaneously separating a high-purity carbon dioxide (CO_2) stream from the reactor for capture. The project goal is to design and fabricate CCDP membranes with improved CO_2 permeance and mechanical strength for testing in a laboratory-scale reactor with simulated coal-derived syngas, with results informing a mathematical model used to support process design and a techno-economic analysis (TEA) for a scenario of incorporation of a CCDP membrane reactor in a full-scale integrated gasification combined cycle (IGCC) plant.

technical goals

- Synthesize chemically and thermally stable CCDP membranes with CO_2 permeance greater than 2,000 gas permeation units (GPU) ($6.5\text{x}10^{-7}$ $mol/m^2 \cdot s \cdot Pa$), CO_2/H_2 selectivity greater than 500, and resistant to poisoning from hydrogen sulfide (H_2S) to the extent that CO_2 flux drops less than 5% after 24 hours of exposure to typical levels of H_2S.
- Fabricate tubular CCDP membrane modules suitable for lab-scale WGS reactor operation (i.e., functional and durable at temperatures in excess of 700°C) and at pressures in excess of 20 atmosphere (atm), and experimentally verify performance at simulated syngas flow rate of 0.25 kg per day equivalent to 0.007 kilowatt-thermal (kWth).
- Determine CCDP membrane WGS reactor process conditions/protocols enabling 99% carbon monoxide (CO) conversion for the WGS reaction, 90% CO_2 recovery, 99% purity of the CO_2 permeate stream, and 90% purity of the H_2 retentate stream.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification-based power plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates CO_2-selective CCDP membranes and WGS catalyst. Within the CCDP membrane WGS reactor, CO_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor. This process concept, with the unified CCPD membrane reactor (depicted in callout) replacing the multistage conventional WGS process and amine absorption unit (both within red dotted line), is depicted in Figure 1.

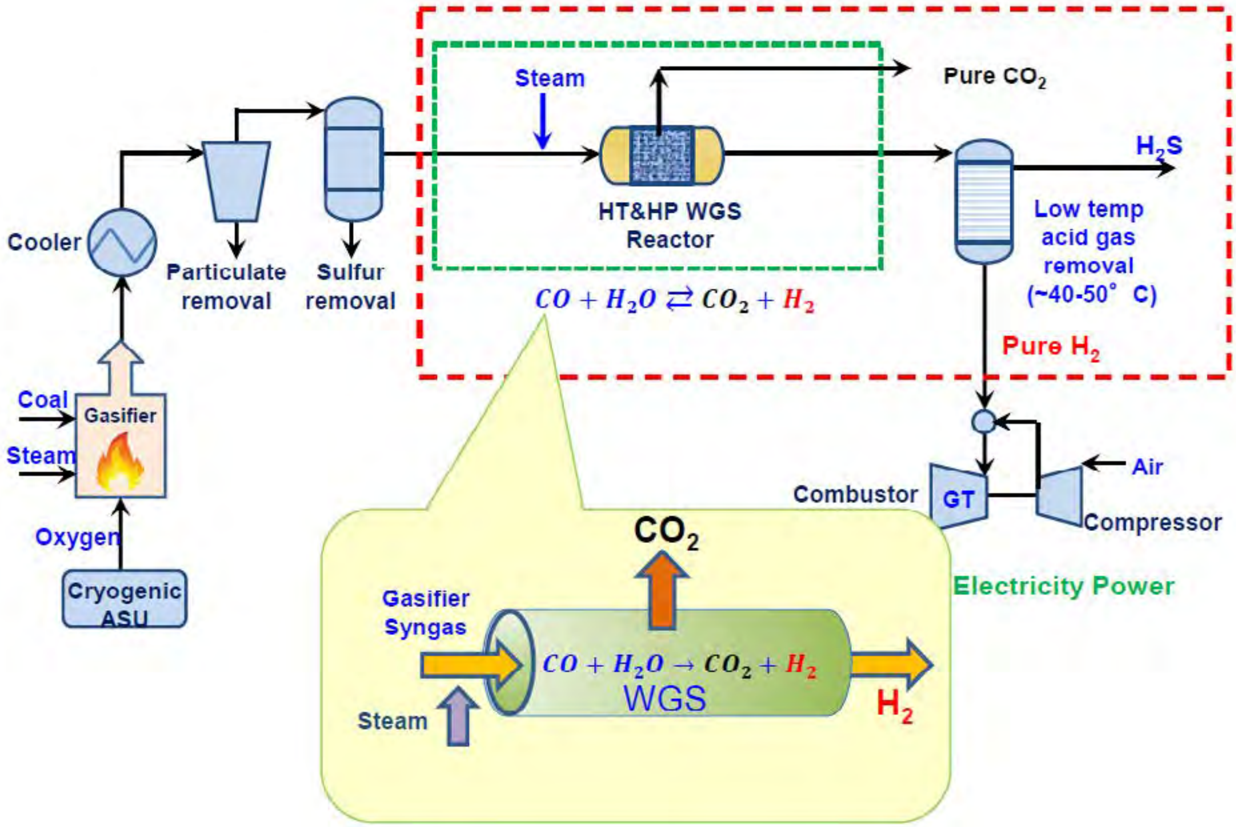


Figure 1: CCDP membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

CCDP membranes are composed of a porous ceramic phase as the structural support matrix, infiltrated with a molten carbonate phase, as illustrated in Figure 2. At working temperatures of 600–900°C, the CCDP membrane possesses extremely high CO_2 selectivity and high CO_2 permeance.

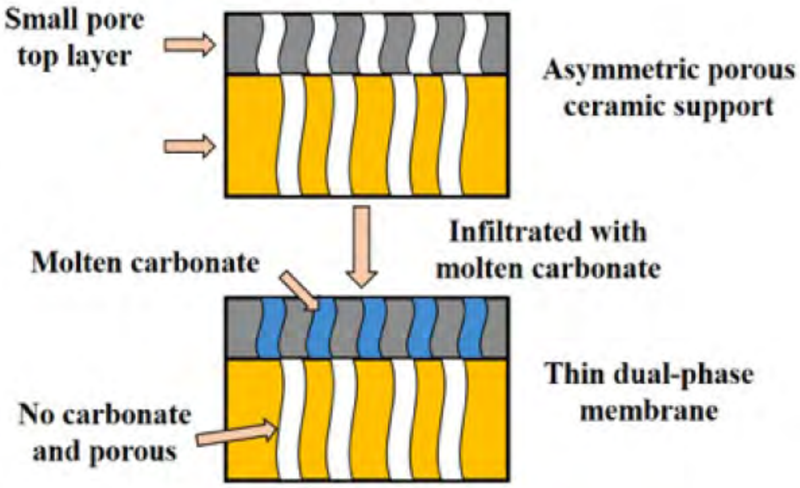


Figure 2: Physical structure of CCDP membrane.

Scanning electron microscopy (SEM) images of actual CCDP membranes are shown in Figure 3. Note that the bright areas in the SEM images are the ceramic phase, while dark zones consist of carbonate mixture. These illustrate the formation of a dense, highly gas-tight dual-phase membrane, which has been verified by pre- and post-infiltration gas permeation measurements.

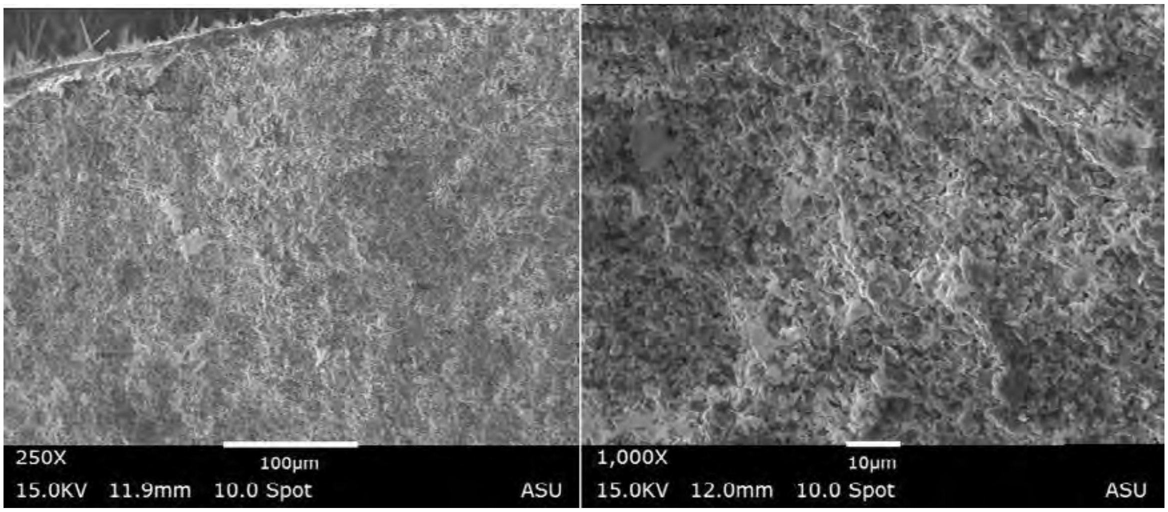


Figure 3: SEM images of CCDP membrane cross-section at 250x (left) and 1,000x (right).

The high selectivity and permeance for CO_2 in the CCDP membrane are a result of the electrochemical transport mechanism illustrated in Figure 4. At elevated process operating temperatures, CO_2 tends to form carbonate ions (CO_3^{2-}) by combining with oxygen ions (O^{2-}), the latter readily transporting through the ionically conducting ceramic phase in the membrane. At the same time, carbonate ions readily transport through the molten carbonate phase in the opposite direction. Syngas on the feed side is at high pressure, resulting in high partial CO_2 pressure on that side. The permeate side is at ambient pressure (and possibly swept), resulting in low partial CO_2 pressure. The CO_2 partial pressure differential provides the driving force for the ionic transport behavior in the membrane. High CO_2 permeance values are expected for the CCDP membrane if the functional layer is made of suitably thin (10–100 µm) ceramic with high oxygen ionic conductivity.

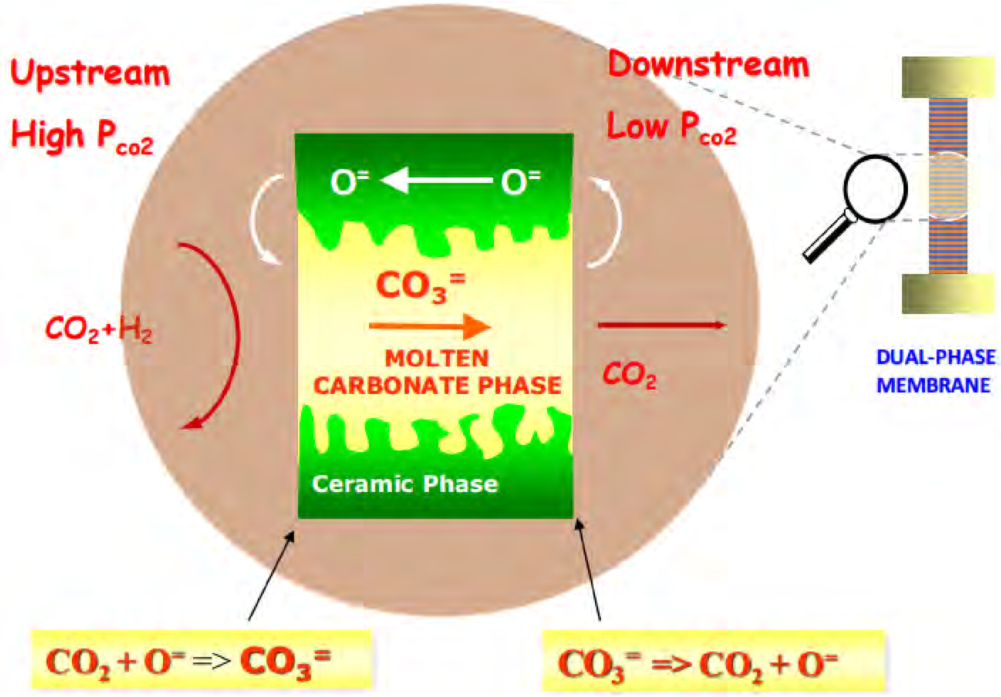


Figure 4: CO_2 separation mechanism in CCDP membrane.

The novel choice of ceramic-carbonate membrane in a WGS reactor overcomes various problems observed with possible alternatives. Theoretically, H_2 could be removed from the WGS reactor through H_2-selective membranes, which would also constitute removal of product of the WGS reaction to drive conversion forward to completion. Inorganic membranes with good H_2 perm-selectivity at high temperatures do exist, and include amorphous microporous carbon; amorphous silica; microporous crystalline zeolite; and dense, perovskite-type, proton-conducting ceramics. However, all of those choices are hampered by one or more serious issues, including insufficient H_2 permeance (particularly at the elevated temperatures involved in the WGS reactor), poor H_2 stability, poor hydrothermal stability, and membrane fabrication difficulty and high cost, which translate into high costs for a membrane WGS reactor solution. Finally, organic membranes of any type are simply incapable of application at the high operating temperatures involved. Considering these shortcomings, a CO_2-selective ceramic-carbonate membrane offers a favorable choice for this application.

An important aspect of technology development for the CCDP membrane concerns optimizing the choices of ceramic and carbonate materials deployed in the membrane, characterization of membrane morphologies and properties, and membrane fabrication. For the ceramic phase of the membrane, desired characteristics include high ionic conductivity, long-term chemical stability in presence of characteristic syngas species and contaminants (particularly H_2S), compatibility with molten carbonate, and controllability of pore size and porosity.

ASU has previously investigated several ceramics for application in the CCDP membrane. The ceramics are in the family of perovskite- or fluorite-structured metal oxides with oxygen vacancy defects:

- $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
- Yttria-stabilized zirconia (YSZ)
- $La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)
- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (Samarium Doped Ceria [SDC]). Note: Figure 3 SEM images are of an SDC-based membrane.
- $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)

ASU has evaluated SDC as a choice for the ceramic phase of the membrane, and has also investigated a Sc_2O_3-doped ZrO_2 (ScSZ). ScSZ avoids the tendency to form compounds with sulfur that is characteristic of cerium (Ce)-containing ceramics. Fabrication methods for the latter have been optimized to deliver the desired microstructure. The ethylenediaminetetraacetic acid (EDTA)-citric acid method is effective; this involves dissolving Sc_2O_3 in nitric acid and mixing with $ZrO(NO_3)_2$, to which EDTA and citric acid are added to the stirred solution in sequence. The solution is pH adjusted and then heated until a clear, viscous gel is formed after water evaporation. The gel is dried and calcined, resulting in almost pure-phase ScSZ with good microstructure.

Tubular membranes for incorporation in modules are formed by establishing thin layers on suitable supports. The ScSZ-based CCDPs are established on BYS support tubes by dip coating them in ScSZ slurry, sintering, and infiltrating the molten carbonate (MC). Essential steps are diagrammed in Figure 5.

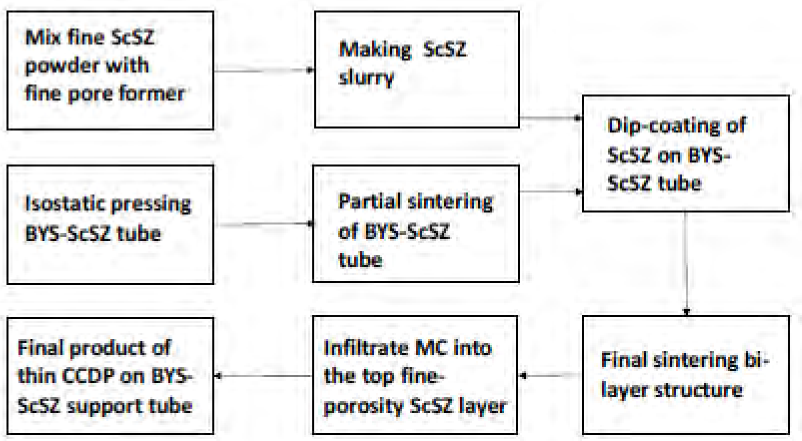


Figure 5: Tubular CCDP membrane fabrication.

For the molten carbonate phase, mixtures of common alkali metal carbonates (i.e., $Li_2CO_3/Na_2CO_3/K_2CO_3$) have been found to be suitable. Varying ratios of the alkali metal carbonates have been evaluated (e.g., a Li/Na/K ratio of 43.5/31.5/25 offers both relatively low melting point [less than 400°C] and good carbonate ion conductivity [1.24 S/cm]). In current work, a binary eutectic mixture of 52% Li_2CO_3 and 48% Na_2CO_3 (MC) is being used with both the SDC and ScSZ ceramics.

Figure 6 depicts the ScSZ-MC membrane tubes along stages of fabrication.

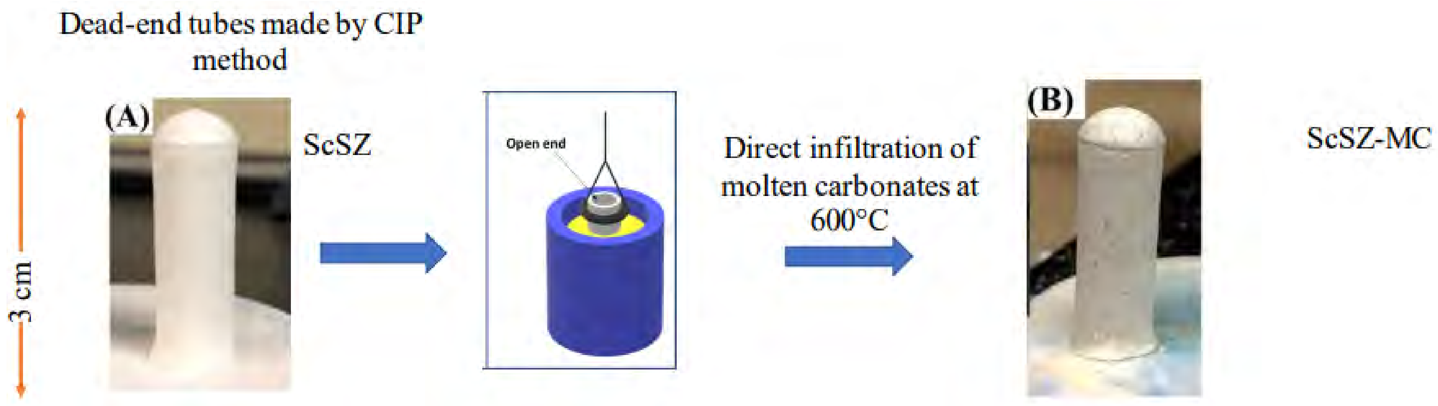


Figure 6: Sc-doped ZrO_2(ScSZ)—(52/48 Li/Na)$_2CO_3$(MC).

An apparatus for characterizing CCDP membrane performance at high temperature and feed pressures has been developed and is operated in laboratory-scale work, as depicted in Figure 7. Synthetic syngas can be mixed up and flowed to the tubular reactor module enclosed in a high-temperature furnace, while resulting gas compositions of permeate and retentate can be measured in a gas chromatograph. The fabrication of the tubular membrane reactor module itself is a challenge, with a notable point of development concerning seals able to withstand the high-targeted operating pressures and temperatures.

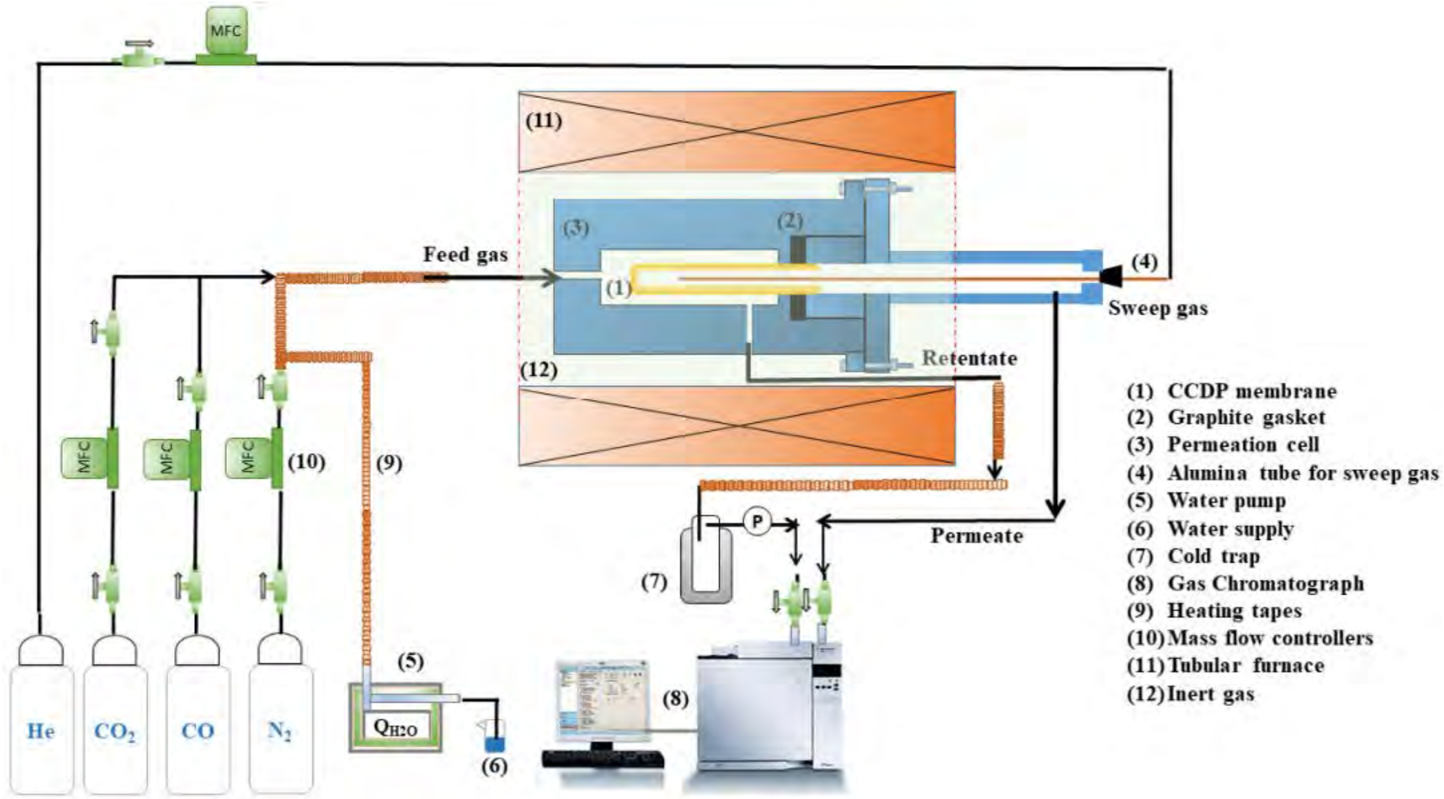


Figure 7: Laboratory-scale apparatus for CCDP membrane CO_2 permeation studies.

With this test bed, various experiments and evaluations are possible, which provide invaluable data for optimizing membrane and module materials and fabrication methods. For example, the reactor module with SDC ceramic infiltrated with Li_2CO_3/Na_2CO_3/K_2CO_3 carbonate mixture (SDC-MC) was evaluated under the following test conditions:

- Temperature: 700–950°C.
- Feed pressure: 1–20 atm.
- Sweep-side pressure: vacuum to 1 atm.

- Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2, 4.5% N_2.
- Feed-side flow rate: syngas 10–30 mL/min and N_2 10 mL/min.
- Steam-to-CO molar ratio: 1.0–3.0.
- Sweep-side flow rate: He 60 mL·min^{-1}.

Results of CO conversion as a function of temperature, syngas flow rate, and ratio of steam to CO are shown in Figure 8, along with behavior of CO conversion, CO_2 permeation, and flux over long-term, steady-state operation. At feed pressure of 7 atm, temperature of 850°C and space velocity of 225 hr^{-1}, CO conversion of 95% has been achieved in the CCDP membrane reactor. Such conversion is significantly higher than the equilibrium CO conversion under the same conditions (62%). The CCDP membrane under such conditions also offers CO_2 permeation flux of 0.56 cm^3(STP)/min.cm^2.

Also, the test bed allows long-term testing to evaluate changes to morphology of CCDP that may occur. For example, Figure 9 shows the high-pressure side of the SDC membrane (left), the SDC-MC infiltrated membrane (center), and the SDC-MC after high-temperature and high-pressure operation.

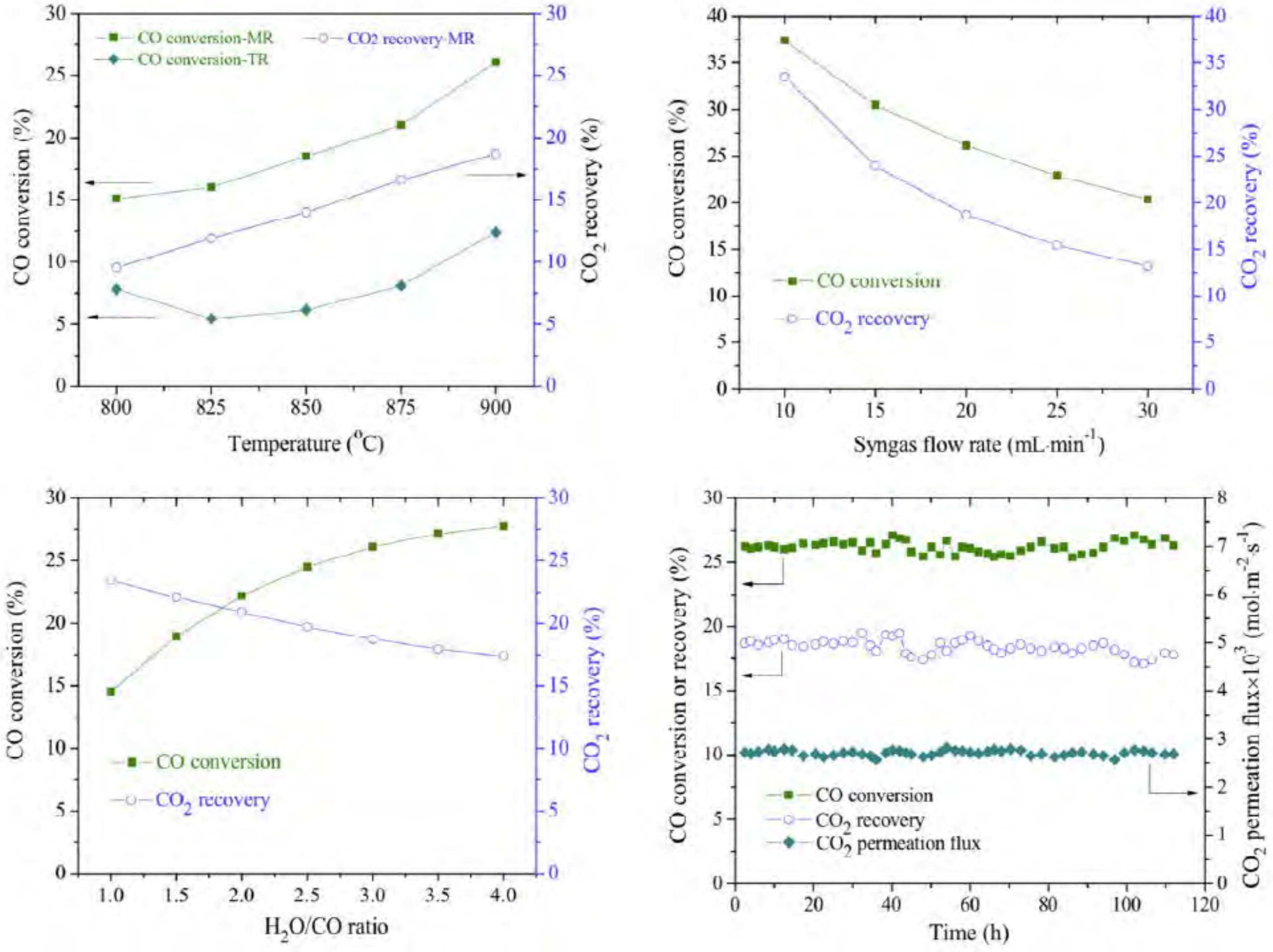


Figure 8: Measurements from tubular CCDP modules in high-temperature WGS testing (1 atm feed).

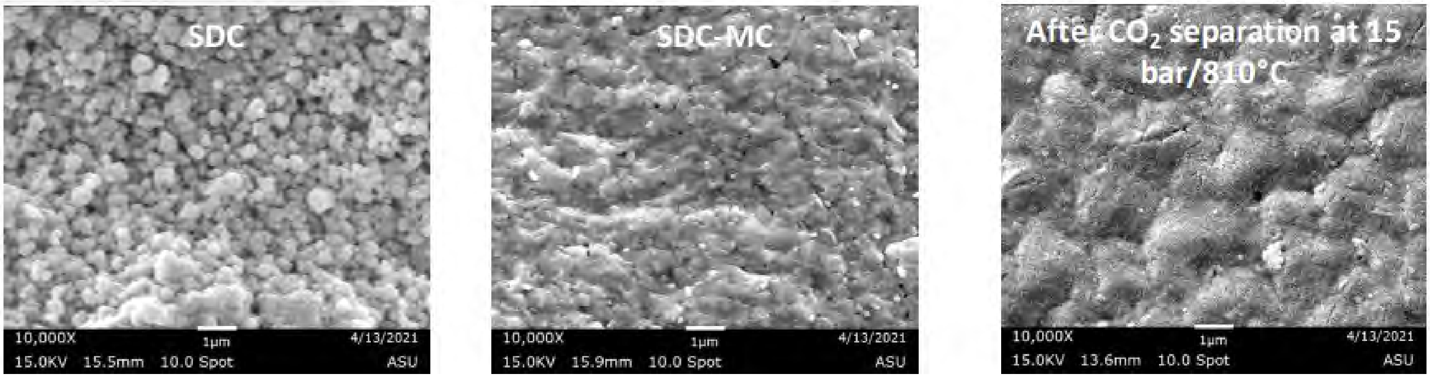


Figure 9: SEM images of high-pressure side of SDC membrane (left); SDC-MC (center); SDC-MC after high-pressure CO_2 permeation (right).

The CCDP membrane reactor has been evaluated for effectiveness in WGS conversion of simulated syngas. The CCDP membrane tubes are surrounded by a Co-Mo-Mg$(AlO_2)_2$-based shift catalyst, as shown in Figure 10. Testing has involved both SDC-MC membranes with catalyst on contaminant-free syngas, and with ScSZ-MC tubular membranes with syngas containing H_2S.

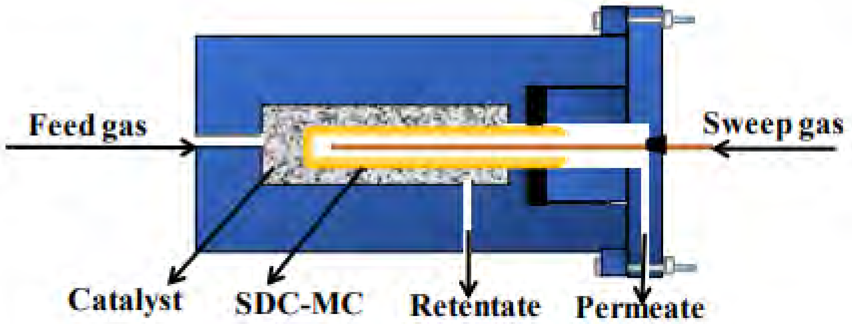


Figure 10: WGS reaction in membrane reactor with Co-Mo-Mg$(AlO_2)_2$-based shift catalyst.

WGS reaction testing with contaminant-free synthetic syngas successfully showed 95% CO conversion in the SDC-MC membrane reactor. The new ScSZ-based, H_2S-resistant CCDP membranes were fabricated in tubular configuration, with CO_2 permeance measured at 2,000 GPU and stability assessed under 30 atm transmembrane pressure drop.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)-(42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)	Sc-doped ZrO_2 (ScSZ) (42.5/32.5/25 Li/Na/K)$_2CO_3$ (MC)
Materials of Fabrication for Support Layer	—	BYS	BYS
Nominal Thickness of Selective Layer	µm	1,500	50-200
Membrane Geometry	—	tubes	tubes
Maximum Trans-Membrane Pressure	bar	1	30
Hours Tested without Significant Degradation	hour	120	>200
Manufacturing Cost for Membrane Material	$/m^2	1,000	500
Membrane Performance			
Temperature	°C	700-900	700-900
CO_2 Pressure Normalized Flux	GPU	300-600	>2,000
CO_2/H_2O Selectivity	—	>500	>500
CO_2/H_2 Selectivity	—	>500	>500

<table>
<tr><td>CO_2/H_2S Selectivity</td><td>—</td><td colspan="2">>500</td><td colspan="2">>500</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="2"><5 ppm</td><td colspan="2">>400 ppm</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="2">mixed-gas</td><td colspan="2">mixed-gas</td></tr>
<tr><td colspan="6">Proposed Module Design</td></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="4">Counter-current</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="4">50-200</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="4">Retentate, H_2-rich flow</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="4">0.005-0.01</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>90</td><td colspan="2">99</td><td>~1</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td>99</td><td colspan="2">90*</td><td>~ 10</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="4">10-30</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="4">~1,000</td></tr>
</table>

* Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 600ºC, the separation of H_2 and CO_2 through CCDP membranes is governed by ionic transport of carbonate ion in MC phase in meso/macropores and oxygen ion in the ceramic phase support.

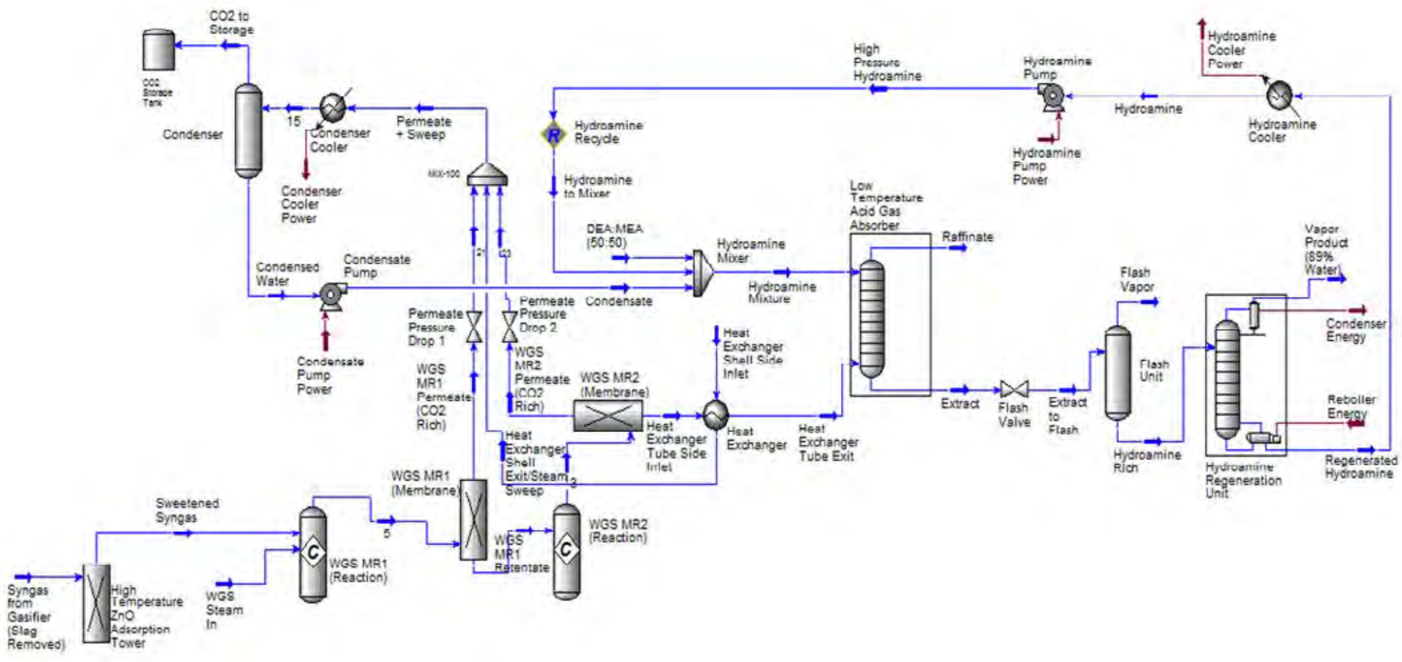
Contaminant Resistance – The developed CCDP membranes have resistance to syngas contaminants such as H_2S.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle is intended to operate in the membrane reactor continuously over 1,000 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere.

Process Design Concept –



Proposed Module Integration – The composition of the gas mixture is assumed:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435	1500	11.6	26.7	0.08	2.8	25.7	33.6	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- WGS reactors containing CO_2-selective membranes to recover CO_2 have potential to achieve higher H_2 delivery to the turbine in an IGCC cycle than if H_2 were being selectively recovered from the syngas stream.
- Carbon dioxide removal through a membrane process in a WGS reactor retains the H_2 at high pressure, maximizing the efficiency of the combustion turbine in an IGCC cycle.
- Tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.

R&D challenges

- ScSZ has poor carbonate wettability making it difficult to infiltrate carbonate and achieve stability.
- Gas leakage through membrane from unsealed pores (imperfect carbonate infiltration).
- High-temperature stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- CCDP thermal stability and poison resistance maintained at high pressures (greater than 20 atm) and temperatures (700–900°C).
- Removal of particulate matter from the hot syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

A laboratory-scale module of the high-temperature and high-pressure CCDP-based WGS membrane reactor has been successfully realized incorporating SDC-MC tubular membranes, which involved development of new seals to avoid leakage. WGS reaction testing with contaminant-free synthetic syngas successfully showed 95% CO conversion in the membrane reactor. The new ScSZ-based, H_2S-resistant CCDP membranes were fabricated with CO_2 permeance measured at 2,000 GPU and stability under 30 atm transmembrane pressure drop. However, the ScSZ has poor wettability with molten carbonate making the ScSZ-MC CCDP membrane unstable. The WGS reaction in H_2S-resistant configuration will be studied with simulated coal-gasified syngas contaminated with H_2S, with CO conversion targeted at 99%.

available reports/technical papers/presentations

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," presented by Jerry Lin, Arizona State University, 2021 NETL Carbon Management Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin_ASU.pdf*

"High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," presented by Oscar Ovalle-Encinia, Arizona State University, 2019 NETL CO_2 Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/O-Ovalle-Encinia-ASU-Ceramic-Carbonate.pdf*

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture," Kick-off meeting presentation, November 2018. *https://netl.doe.gov/projects/plp-download.aspx?id=10558&filename=High+Temperature+Ceramic-Carbonate+Dual-Phase+Membrane+Reactor+for+Pre-Combustion+Carbon+Dioxide+Capture+.pptx*

"High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-combustion Carbon Dioxide Capture," presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/L-Meng-ASU-High-Temperature-Ceramic-Carbonate-Dual-Phase-Membrane.pdf*

Ovalle-Encinia and J. Y.S. Lin, "High-pressure CO_2 permeation properties and stability of ceramic-carbonate dual-phase membranes", *J. Membr. Sci*., 646, 120249 (2022).

M Anderson & YS Lin, Proc. ICIM 2006, pp. 678-681 (2006); J. Membr. Sci. 357, 122 (2010).

Transformational Membranes for Pre-Combustion Carbon Capture

primary project goal

The Ohio State University's (OSU) goal was to develop cost-effective design and fabrication methods for a novel amine-containing membrane to capture carbon dioxide (CO_2) from coal gasification-derived syngas, assuming a single-stage membrane process utilizing modules in commercial spiral-wound configuration. Project scope of optimization and scale-up of transformational membranes with high CO_2/hydrogen (H_2) selectivity and CO_2 permeance, plus testing of spiral-wound membrane modules using simulated syngas, facilitated progress toward CO_2 capture with improved performance to meet U.S. Department of Energy (DOE) targets for cost of electricity (COE) and efficiency in advanced power generation plants.

technical goals

- Synthesize and characterize membranes, scale-up the best performing membrane using a continuous roll-to-roll fabrication method, and fabricate prototype membrane modules with approximate membrane area of 800 cm^2.
- Establish module stability by testing of the modules at 31.7 bar and 107°C for at least 200 hours on simulated syngas at 34 standard liter per minute (slpm) flowrate.
- Enable CO_2 capture at 95% CO_2 purity, with greater than 99% H_2 recovery from syngas.
- Optimize processes for integrating membrane modules into integrated gasification combined cycle (IGCC) with carbon capture, showing potential via techno-economic analysis (TEA) to reduce the COE by 30% relative to conventional/baseline approaches (Selexol).

technical content

Many common polymeric membranes for gas separations are based on a solution-diffusion mechanism, which makes these polymeric membranes simple to fabricate and low in cost. However, these membranes face considerable performance limitations, along with the inevitable trade-off between selectivity and permeability. Figure 1 illustrates this for polymer membrane separation of CO_2 and H_2. In order to exceed the upper bound, utilization of selective facilitated transport is essential.

OSU's technological approach for the membrane focuses on a CO_2-selective and permeable membrane layer on top of a polymer support, with amino groups added to facilitate CO_2 transport. The basic structure of the membrane is depicted in Figure 2. Because this membrane is to be deployed to remove CO_2 from coal-derived syngas, it is required to exhibit chemical stability to hydrogen sulfide (H_2S) gas, which is always present in at least trace amounts of coal syngas. Also, it is preferred that it can function at elevated temperature, which is characteristic of warm syngas cleanup regimes. The top layer of the membrane is the selective layer containing polymeric and small amines, while the support layer is made of

program area:

Point Source Carbon Capture

ending scale:

Laboratory Scale

application:

Pre-Combustion Power Generation PSC

key technology:

Membranes

project focus:

Amine-Containing Polymeric Membranes for CO_2 Capture from Coal Syngas

participant:

The Ohio State University

project number:

FE0031635

predecessor projects:

N/A

NETL project manager:

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principal investigator:

W.S. Winston Ho
The Ohio State University
ho.192@osu.edu

partners:

American Electric Power;
Microdyn-Nadir US Inc.

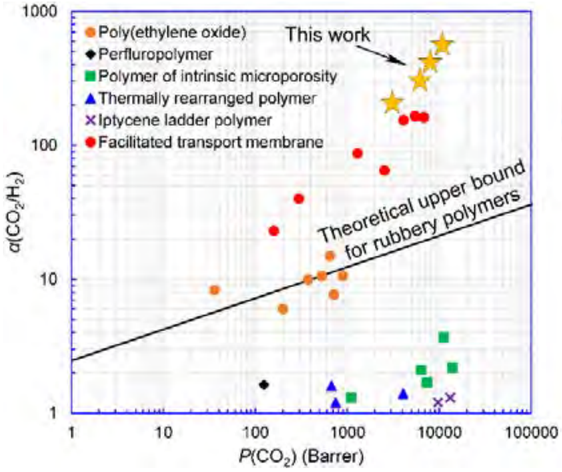
start date:

10.01.2018

percent complete:

100%

nanoporous polysulfone, which is both highly permeable to gases and is mechanically robust. Some details of composition of the selective polymer layer are proprietary.



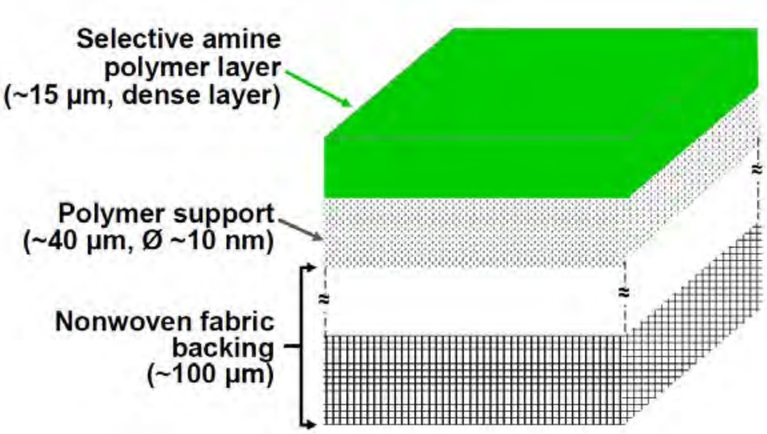


Figure 1: Typical performance of polymer membranes for CO_2/H_2 separations.

Figure 2: Membrane structure.

The facilitated transport mechanism involves enhancement of CO_2 transfer or flux through the membrane via chemical reaction with amino groups located in the selective layer. The reversible reaction of CO_2 with amino groups is as follows:

$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + HCO_3^-$$

The facilitated transport mechanism is depicted in Figure 3. Other non-acid gases, including H_2, carbon monoxide (CO), methane (CH_4), and nitrogen (N_2), are non-reactive with the membrane, and can therefore only slowly permeate through the membrane by a physical solution-diffusion mechanism. This results in high selectivities for CO_2 relative to these non-reactive gases. In contrast, the acid gas H_2S has an even higher rate of permeation through the membrane than CO_2. This means that high levels of sulfur removal from the syngas will be accomplished in a membrane separation module, with less than 10 parts per million (ppm) H_2S remaining in the syngas retentate on the feed side. The CO_2 permeate does require further treatment to remove the H_2S from the CO_2 before the latter could be stored or used.

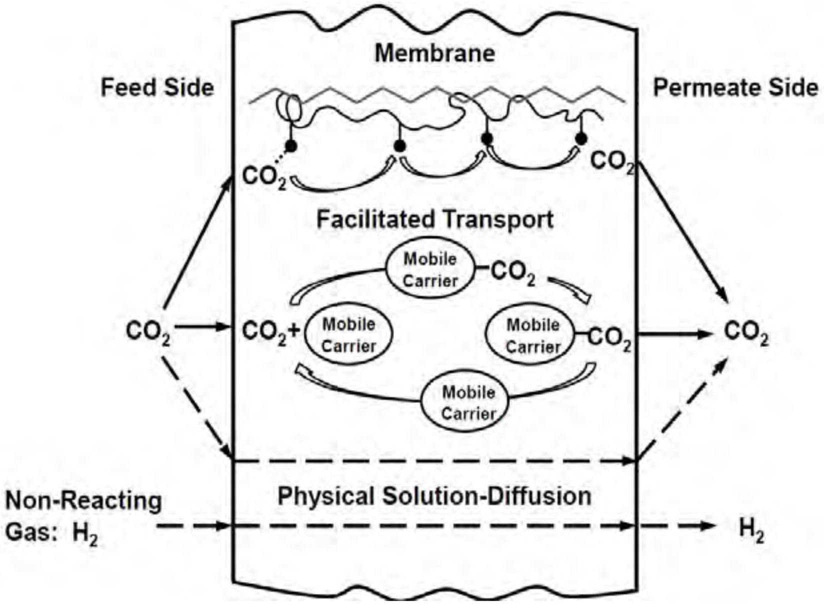


Figure 3: Mechanism of facilitated transport.

Process Scenario

One scenario for an overall plant process context is depicted in Figure 4. In order to enable 90% carbon capture in coal gasification-based IGCC processes, the preferred method is oxygen-based pressurized gasification resulting in low nitrogen content raw syngas. Syngas is shifted via the water-gas shift (WGS) reaction in a WGS unit, resulting in syngas containing large fractions of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane unit. Carbon dioxide and H_2S permeate to the low-pressure permeate side of the membrane unit; H_2S can be subsequently separated from the permeate mixture in a single-stage Selexol unit, while the purified CO_2 is compressed and sent to storage. The high-pressure syngas retentate serves as fuel gas for a combustion turbine.

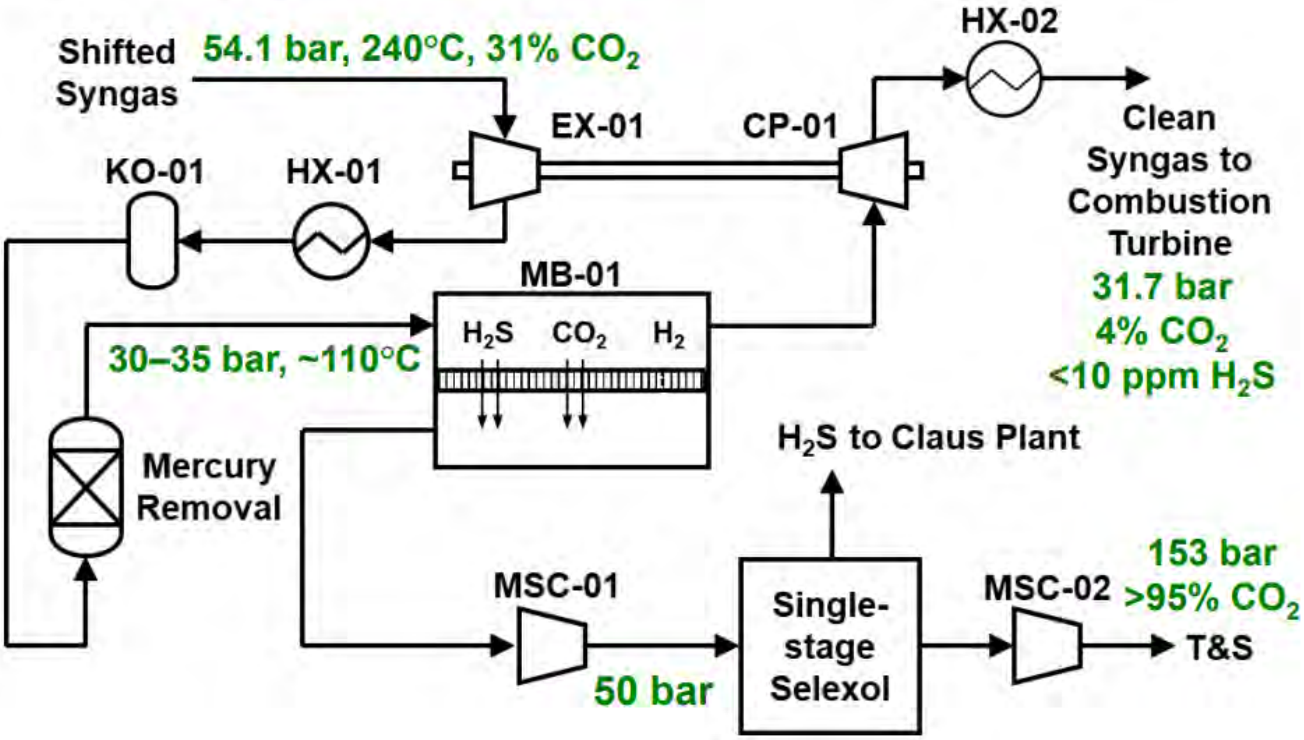


Figure 4: Process integration of membrane separation unit.

For industrial applications, it is intended that the polymeric membrane would be packed into spiral-wound membrane modules, a commonly used module design for current commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 60% of the membrane market for CO_2 removal from natural gas. Figure 5 shows the fabrication procedure and photos of the prototype spiral-wound element and assembled membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers. OSU has continuously fabricated thin-film-coated membranes at 14-inch width, which were incorporated in prototype spiral-wound membrane modules used for testing and evaluation. Modules with membrane areas of 0.08 and 0.16 m^2 (Type I and Type II, see below) were fabricated.

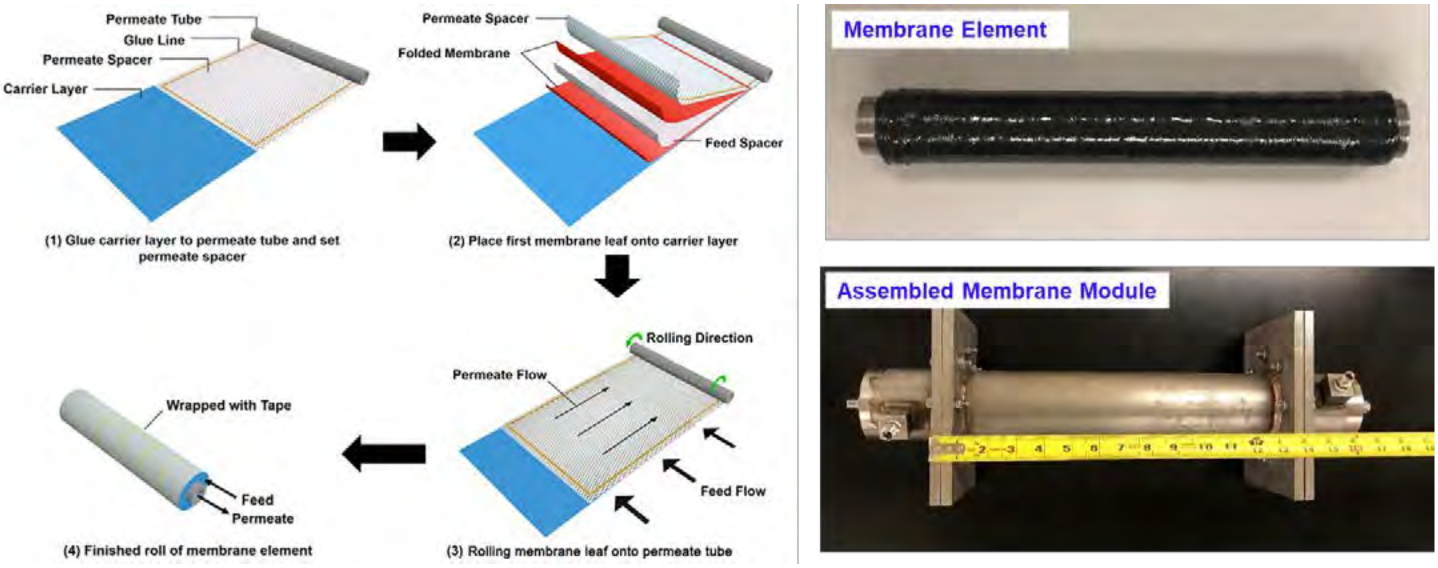


Figure 5. Procedure of single-leaf spiral-wound membrane element fabrication (left). Photos of an 0.08-m² prototype spiral-wound membrane element and assembled membrane module (right).

Membrane Optimization

A major technology development focus was improving performance of the membrane chiefly in terms of increasing CO_2 permeance (while maintaining CO_2/H_2 selectivity in the range of greater than 100). Approaches for improving permeance included the following:

- Using sterically hindered amines as CO_2 carriers: Comparing the mechanisms of reaction of CO_2 with both unhindered and hindered amines, the latter can double the CO_2 carrying capacity. Figure 6 shows the CO_2 permeance and CO_2/H_2 selectivity of a membrane incorporating the Type II carrier, which is a hindered amine. The hindered amine shows high selectivity at low CO_2 partial pressures (< 8 bar), while still maintaining acceptable permeance values. Also, H_2S/CO_2 selectivity of ~4 is attained, which allows a substantial degree of separation of H_2S resulting in 6 ppmv concentration of H_2S in the H_2 retentate.
- Incorporating certain molecular substituents or side chains in the membranes' molecular structure to improve facilitated transport: Also shown in Figure 6 is a membrane containing the Type I carrier, an amine-containing hydroxyethyl moiety. This membrane shows a CO_2/H_2 selectivity greater than 100 even at high CO_2 partial pressures (up to 14 bar).
- Tuning the composition of the membrane polymers: Different carrier structures in the membrane have effects on performance. It is possible to optimize membrane polymer composition for different ranges of CO_2 partial pressures.
- Incorporation of nanofillers: Linkages between molecular chains are not rigid in the polymer membrane. This means that at working temperatures (e.g., 107°C), the crosslinked polymer network is rubbery and compressible. At high syngas pressure, induced hydrostatic compression reduces the polymer free volume, causing reduced gas diffusivity through the polymer. In order to mitigate the membrane compaction, nanofillers can be dispersed in the polymer network as reinforcement. Nanofiller in the form of perforated carbon nanosheet has been economically synthesized in-house at OSU and utilized for this purpose.

Ultimately, targets for membrane fabrication and performance were met, with CO_2 permeance in the range of 275–350 GPU and CO_2/H_2 selectivity in the range of 120–140 achieved. Also, the targeted scale-up of fabricated membranes and size/capacity of the prototype spiral-wound modules were achieved.

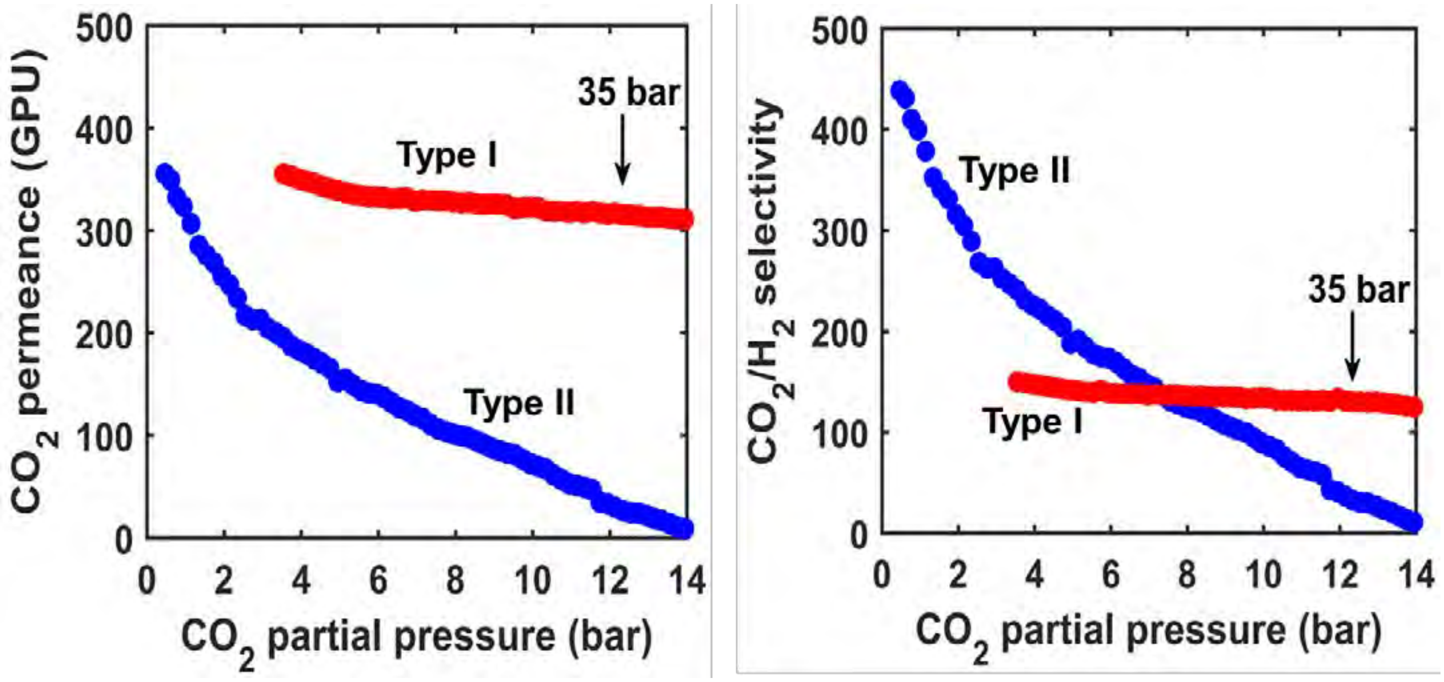


Figure 6. CO_2 permeances and CO_2/H_2 selectivities of membranes incorporating the Type I and Type II mobile carriers in simulated syngas at 107ºC and 35 bar.

Spiral-wound modules incorporating optimized Type I and Type II membranes were tested in simulated syngas at 107ºC and 35 bar. The purity of CO_2 permeate and H_2 recovery were measured as functions of extent of CO_2 recovery, and the results are depicted in Figure 7. Note that the Type II modules with twice the membrane area of Type I enable higher purities and H_2 recovery for given CO_2 recoveries. Experimental results agree well with theoretical calculations.

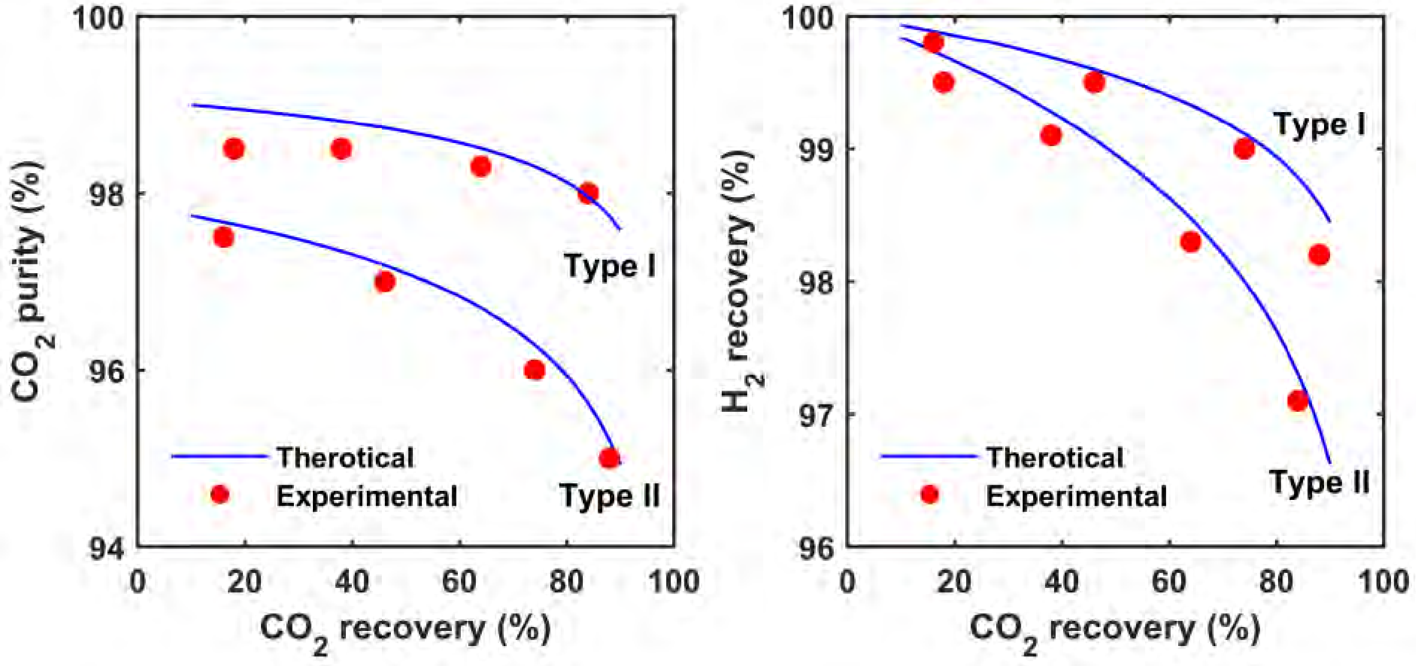


Figure 7. Spiral-wound module performance testing and evaluation.

The Type I and Type II modules OSU had developed were connected in a series and tested on simulated syngas for 200 hours. The membrane modules yielded an average CO_2 purity of 95.2% with a H_2 recovery of 99.3% and remained stable, with no discernable loss of separation performance to the end of the period of testing. The 200-hour stability demonstrated that the mobile carriers possess a negligible volatility in the polymeric membrane (which minimizes the possibility of loss through volatility), that the membranes are mechanically stable under the high syngas pressure, and that the polymer matrix is fully rubbery and not subject to a conformational relaxation (i.e., no physical aging is expected).

A TEA of a single-stage membrane process based on the OSU-facilitated transport membrane in an IGCC plant context was performed. This was based on an IGCC plant baseline as documented in the 2019 DOE Cost and Performance Baseline document (Revision 4). OSU found that implementation of the membrane-based capture results in a COE of \$124.4/MWh. This value corresponds to a COE increase of 15.3%, which is significantly lower (i.e., 54.5%) than the benchmark two-stage Selexol process given in the DOE baseline (i.e., COE increase of 33.6%).

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymer with amino groups	polymer with amino groups
Materials of Fabrication for Support Layer	—	polysulfone	polysulfone
Nominal Thickness of Selective Layer	µm	~15 – 25	15 – 25
Membrane Geometry	—	spiral wound	spiral wound
Maximum Trans-Membrane Pressure	bar	35	35
Hours Tested without Significant Degradation	—	200	≥200
Manufacturing Cost for Membrane Material	\$/m²	~54	≤54
Membrane Performance			
Temperature	°C	107	107

CO_2 Pressure Normalized Flux	GPU	355	275 – 350	
CO_2/H_2O Selectivity	—	1	1	
CO_2/H_2 Selectivity	—	150	120 – 140	
H_2S/CO_2 Selectivity	—	4 – 7	3	
Sulfur Tolerance	ppm	>6,000	>6,000	
Type of Measurement	—	mixed gas	mixed gas	
Proposed Module Design				
Flow Arrangement	—		Counter-current	
Packing Density	m^2/m^3		2000	
Shell-Side Fluid	—		Retentate, H_2-rich flow	
Syngas Gas Flowrate	slpm		50	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	95.2	1.1
H_2 Recovery, Purity, and Pressure	%/%/bar	99.3	94	35
Pressure Drops Shell/Tube Side	psi/m		1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$		87.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-10} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport mechanism.

Contaminant Resistance – Membrane is tolerant to greater than 6,000 ppm H_2S.

Syngas Pretreatment Requirements – Thermal expansion for mild syngas cooling, and filtration to remove any particulate matter.

Membrane Replacement Requirements – Spiral-wound membrane elements are expected to be replaced every five years.

Waste Streams Generated – Elemental sulfur recovered from the captured H_2S and CO_2 stream via the Claus process.

Proposed Module Design – See Figures 4 and 5. The pressure, temperature, and composition of the gas entering the membrane module are as follows:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
507.6	224.6	39.6	—	—	—	56.1	3.7	6065

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	N/A	N/A
Cost of Carbon Avoided	\$/tonne CO_2	N/A	N/A
Capital Expenditures	\$/MWhr	73.4	78.7
Operating Expenditures	\$/MWhr	51.0	54.6
Cost of Electricity	\$/MWhr	124.4	133.3

Definitions:

Please provide data from economic analysis previously performed for your project.

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 4.

Scale of Validation of Technology Used in TEA – Laboratory testing.

Qualifying Information or Assumptions –

- The membrane element cost is assumed as \$5/ft^2 membrane area based on the current market price for spiral-wound element in natural gas sweetening. A cost of \$0.5/ft^2 membrane area is used for the module housing according to RO applications with a feed pressure up to 60 bar.
- The membrane life is assumed as four years. Based on the membrane element cost of \$5/ft^2, the annual membrane replacement cost is \$1.25/ft^2. This cost is included in the variable cost.

technology advantages

- The simplicity of the amine-polymer membrane structure lowers its manufacturing cost.
- Membrane modules do not contain moving parts or involve chemical reaction, simplifying operation and maintenance.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.

- Spiral-wound module configuration affords minimal pressure drop, helping energy efficiency.
- The membrane capture system can operate warm/hot to reduce the need for heat exchange (e.g., membrane modules operate at a higher temperature and pressure than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and lowering the energy and capital cost required to convert captured CO_2 to liquid).
- The membrane can remove H_2S simultaneously with CO_2, resulting in low-sulfur H_2 for combustion or chemical synthesis.

R&D challenges

- Increasing the CO_2 permeance of the membrane.
- Assuring polymer support performance and properties.
- Choice of spacer and glue for high-temperature membrane module fabrication.
- Scale-up and integration issues are possible given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

- The project was completed in March 2022.

available reports/technical papers/presentations

Y. Han and W. S. W. Ho, "Facilitated Transport Membranes for H_2 Purification from Coal-Derived Syngas: A Techno-Economic Analysis," *J. Membr. Sci*., 636, 119549 (2021).

"Design of Amine-Containing CO_2-Selective Membrane Process for Carbon Capture from Flue Gas," Yang Han and W.S. Winston Ho, Industrial & Engineering Chemistry Research, 59, 5340–5350 (2020).

"Transformational Membranes for Pre-combustion Carbon Capture," presented by Winston Ho and Yang Han, The Ohio State University, 2021 NETL Carbon Management Research Project Review Meeting, August 16, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Ho.pdf*

"Amine-Containing Membranes with Functionalized Multi-Walled Carbon Nanotubes for CO_2/H_2 Separation," Yutong Yang, Yang Han, Ruizhi Pang, and W.S. Winston Ho, Membranes, 10, 333 (2020).

"Transformational Membranes for Pre-combustion Carbon Capture," NETL Budget Period 1 Project Review Meeting (virtual), Pittsburgh, PA, February 18, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10563&filename=Transformational+Membranes+for+Pre-combustion+Carbon+Capture.pdf*

"Facilitated Transport Membranes with Tunable Amine-CO_2 Chemistry for Highly Selective CO_2/H_2 Separation," presentation by Yang Han and W.S. Winston Ho, 2019 AIChE (American Institute of Chemical Engineers) Annual Meeting. Orlando, FL, November 2019, Paper 750a.

"Transformational Membranes for Pre-combustion Carbon Capture," presentation by Winston Ho and Yang Han, The Ohio State University, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Precombustion-Membranes.pdf*

"Transformational Membranes for Pre-combustion Carbon Capture," project kickoff meeting presentation, November 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10567&filename=Transformational+Membranes+for+Pre-combustion+Carbon+Capture.pdf*

"Transformational Membranes for Pre-combustion Carbon Capture," Poster presentation by Yang Han, The Ohio State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Membranes.pdf*

Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

primary project goal

The goal of this State University of New York (SUNY)–Buffalo project is to develop scalable membrane technology by engineering polymers to achieve superior hydrogen (H_2)/carbon dioxide (CO_2) separation properties in readily fabricated and easily deployed membranes for capture of CO_2 from coal-derived syngas. Specifically, the approach is to derive carbon molecular sieve (CMS) membranes from polybenzimidazole (PBI) doped with polyprotic acids, which should offer high H_2 permeance and H_2/CO_2 selectivity while retaining robust chemical stability at elevated operating temperature.

technical goals

- Develop CMS hollow fiber membranes (HFMs) having a H_2 permeance of 1,000 gas permeation units (GPU) and an H_2/CO_2 selectivity of 40 at 200–300°C.
- Fabricate small membrane modules and demonstrate membrane performance and durability via testing of the modules under simulated syngas flow at 0.01 kilowatt-electric (kWe) equivalency for 120 hours.
- Characterize a CMS membrane-based system able to capture 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches (Selexol) in the context of an integrated gasification combined cycle (IGCC) plant scenario.

technical content

Conventional methods for pre-combustion carbon capture consist mainly of solvent-based processes such as Selexol and Rectisol. Although enabling high levels of capture at high gas purity, these processes have high capital and operating costs and result in severe energy penalties. Membrane-based carbon capture is of continued interest as an alternative, given its potential advantages in simplicity, lower costs, and potential for large savings in energy use. Among membranes for separation of CO_2 from syngas, inorganic membranes such as palladium alloys, ceramics, metal-organic frameworks (MOFs), and graphene oxide have been evaluated, given their excellent H_2/CO_2 separation properties. However, they are faced with challenges in the cost and reliability, scale-up of membrane production, and module fabrication. In contrast, polymer-based membranes are much easier to implement than inorganic membranes, provided that the membrane materials demonstrate suitable separation properties. Production scale-up and module fabrication using polymeric membranes have been widely practiced, creating a substantial engineering knowledge base across

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-Combustion Power Generation PSC

key technology:
Membranes

project focus:
Carbon Molecular Sieve Hollow Fiber Membranes With Coal Syngas

participant:
State University of New York – Buffalo

project number:
FE0031636

predecessor projects:
N/A

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partners:
Los Alamos National Laboratory; Trimeric Corporation

start date:
10.01.2018

percent complete:
95%

the polymer membrane industry. Building on this foundation, this work targeted development of scalable membranes by engineering polymers to achieve superior H_2/CO_2 separation properties.

Most work in H_2/CO_2 gas separations by polymeric membrane materials relies solely on strong size-sieving derived from the rigid polymer chains. Polymers available commercially in this class include examples like poly(p-phenylene oxide) (PPO), Matrimid, poly(bisphenol-A sulfone) (PSF), and cellulose acetate (CA). However, the commercially available polymers have low H_2 diffusivity and permeability, are limited by the permeability/selectivity trade-off, and are well below the Robeson upper bound, as illustrated in Figure 1.

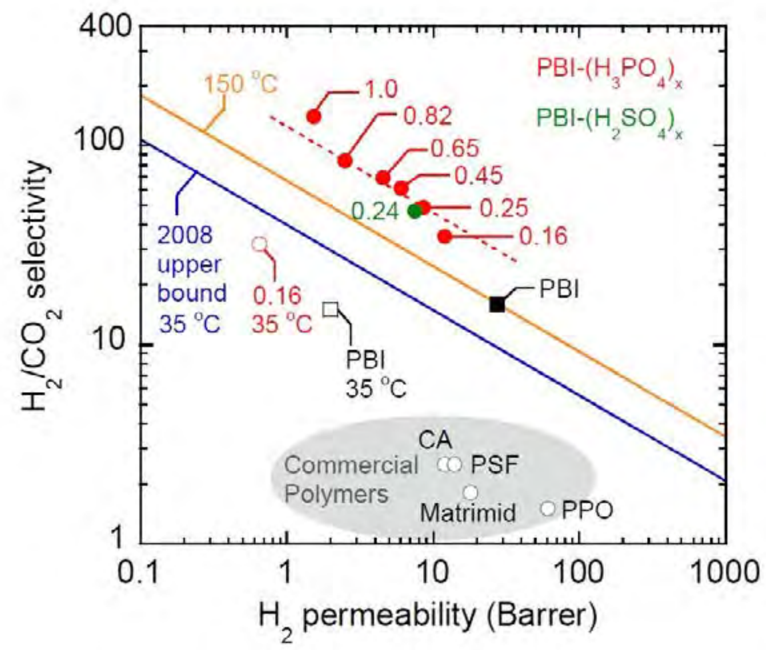

Figure 1: Pure-gas H_2/CO_2 separation performance of $PBI-(H_3PO_4)_x$ (x = 0.16-1.0) and $PBI-(H_2SO_4)_{0.24}$ at 150°C versus Robeson's upper bound at 35°C and 150°C.

The SUNY team has demonstrated considerable improvement in polymer membrane performance by doping the polymer PBI with polyprotic acids such as phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to improve the size-sieving ability and H_2/CO_2 separation properties at 120–180°C. As shown in the upper part of Figure 1, increasing the H_3PO_4 doping level (defined as the molar ratio of H_3PO_4 to the PBI repeating units) decreases the pure-gas permeability and drastically increases the H_2/CO_2 selectivity at 150°C. For example, plain PBI shows an H_2/CO_2 selectivity of 16, while $PBI-(H_3PO_4)_{1.0}$ exhibits a remarkable selectivity of 140, which is much higher than that of any previously studied polymers. Phosphoric acid can strongly interact with multi-PBI chains via proton transfer from the acid to imidazole rings of PBI and hydrogen bonding, and thus it crosslinks the PBI. In comparison, a monoprotic acid such as hydrogen chloride (HCl) does not crosslink the PBI chains and has minimal effect on H_2/CO_2 separation properties.

SUNY's approach was to start with the already strongly size-sieving polymers (i.e., PBI doped with polyprotic acids [PPA]), and then carbonize them (by heating/pyrolysis at 500–800°C in inert nitrogen [N_2] for at least an hour) to increase both permeability and selectivity into a range suitable for commercial deployment. This approach is diagrammed in Figure 2, showing PBI being doped with the PPA pyrophosphoric acid, and then carbonized by pyrolysis. Carbonizing the acid-doped PBI results in CMS in which microcavities form, tending to increase gas permeability, and ultra-microporous necks increasing size-sieving ability.

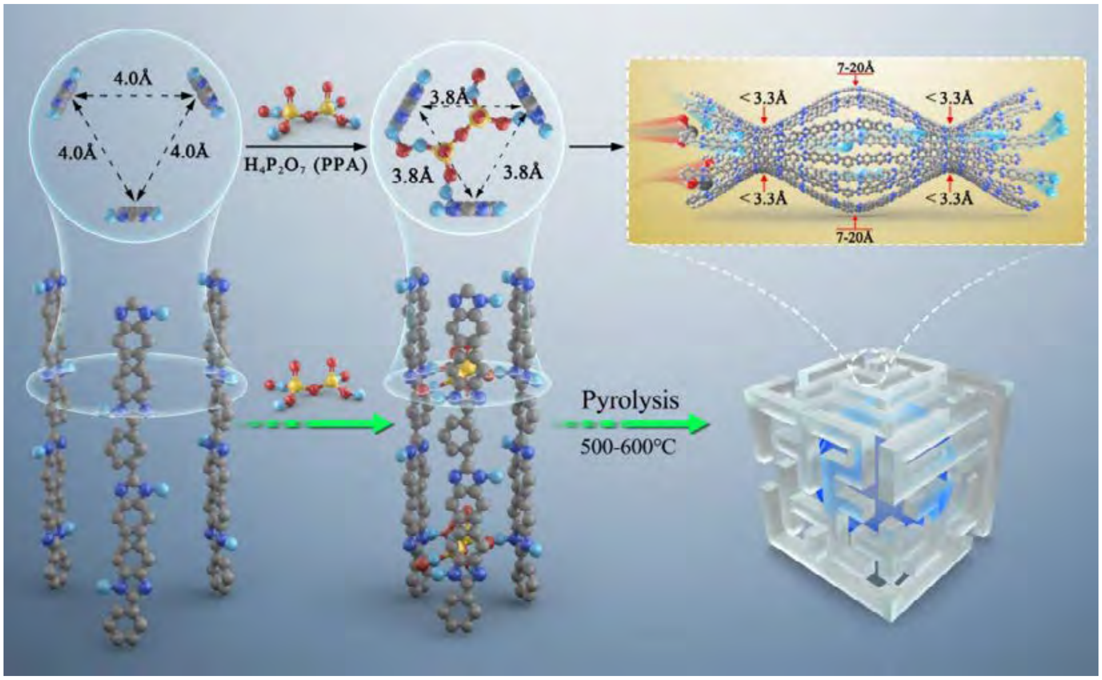

Figure 2: Steps to CMS membranes derived from PBI doped with polyprotic acids.

In past work, CMS membranes were made by carbonizing plain PBI. The pyrolysis increases the porosity and generates graphite-like structure. As shown in Figure 3 in blue, the carbonization of PBI substantially increases H_2 permeability while retaining or slightly increasing H_2/CO_2 selectivity at 100°C. All CMS samples have exhibited H_2/CO_2 separation properties above the upper bound. For example, pure PBI exhibits an H_2 permeability of 12 Barrer and an H_2/CO_2 selectivity of 14 at 100°C, while the CMS prepared by pyrolysis of PBI at 800°C shows an H_2 permeability of 670 Barrer (which is 50 times higher than pure PBI) and an H_2/CO_2 selectivity of 18 at 100°C.

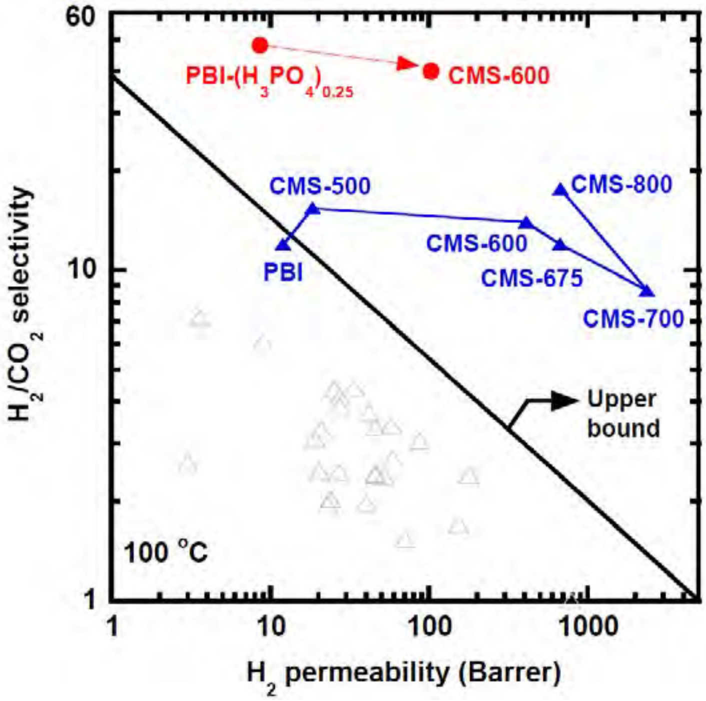

Figure 3: Improvement in membrane performance upon carbonization to CMS.

The SUNY team hypothesized that the CMS membranes would be able to meet targeted separation properties (H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40) if the starting polymers were PBI doped with polyprotic acids with strong size-sieving ability. For example, PBI-$(H_3PO_4)_{0.25}$ exhibits an H_2 permeability of 8.6 Barrer and an H_2/CO_2 selectivity of 48 at 150°C. The pyrolysis at 600°C increases the permeability to 100 Barrer while retaining an H_2/CO_2 selectivity of 40 at 100°C, as shown in red in Figure 3. During the pyrolysis, the H_3PO_4 gradually decomposes to polyphosphoric acid ($(HPO_3)_n$), retaining the rigid chains and strong molecular size-sieving ability.

Results of optimization of the acid type, composition, and pyrolysis temperature are depicted in Figure 4. The left side depicts results of doping with phosphoric acid at different proportions, while the right side shows results of doping with pyrophosphoric acid at different proportions, and before and after carbonization (respectively blue and red). A pyrolysis temperature of 600°C was found to be optimal. SUNY was able to achieve H_2 permeability of 200 Barrer with an H_2/CO_2 selectivity of 40 for pyrophosphic acid-doped, 600°C pyrolized PBI-PPA_x at x values of about 0.25.

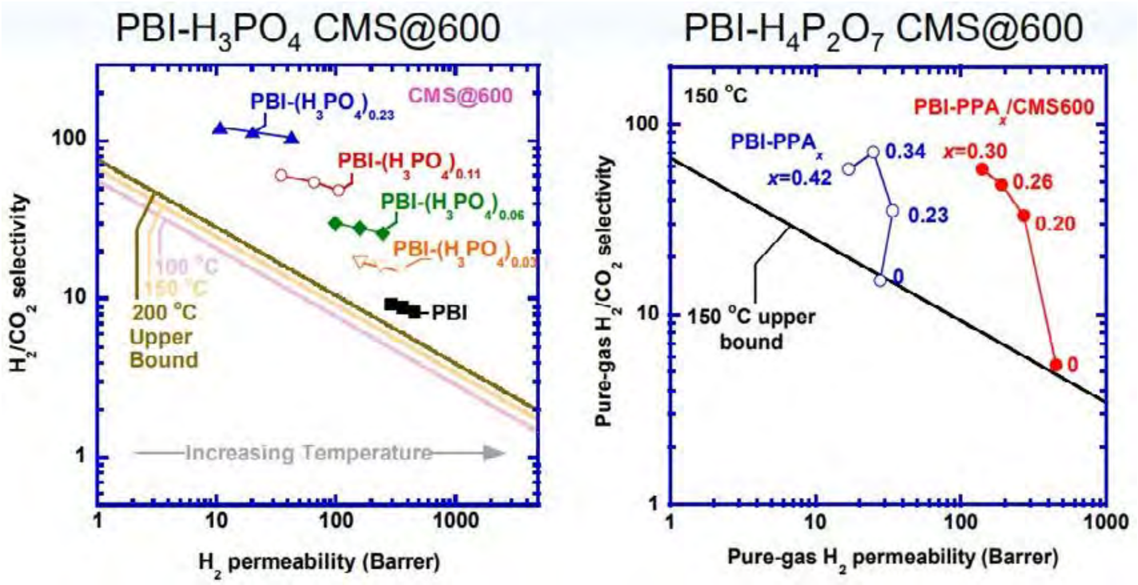

Figure 4: Improvement in membrane performance upon carbonization to CMS.

With this degree of permeability, HFMs with a selective layer thickness of 0.2 µm will achieve an H_2 permeance of 1,000 GPU and an H_2/CO_2 selectivity of 40. Los Alamos National Laboratory (LANL) has successfully fabricated nearly defect-free PBI HFMs with a 0.2 µm selective layer. Figure 5 shows images of (a) a base PBI HFM and (a') carbonized hollow fiber. This illustrates that the carbonized fiber retains the porous support morphology of the starting fiber.

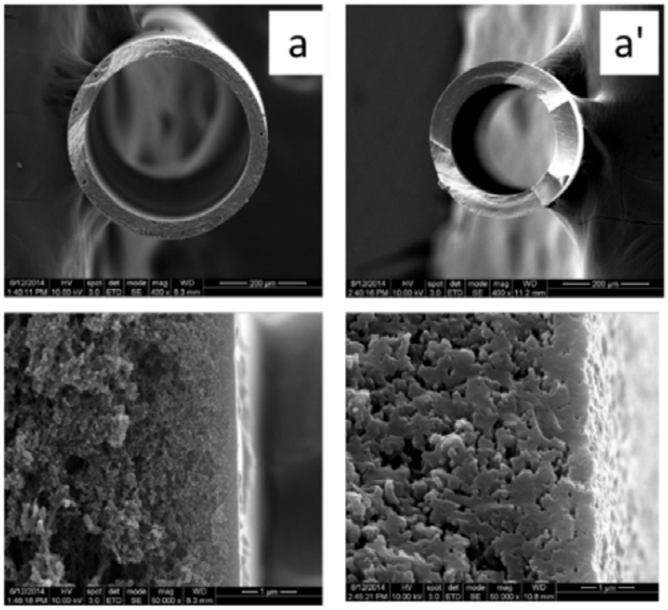

Figure 5: Scanning electron microscopy (SEM) images of PBI hollow fibers, before (left) and after (right) carbonization.

CMS membranes are intended for incorporation in hollow fiber modules for deployment in gas separation systems. LANL used the hollow fiber spinning system depicted in Figure 6 to fabricate the hollow fibers. A custom micro-machined spinneret forms the fiber. The steps resulting in CMS carbon fibers are also diagrammed.

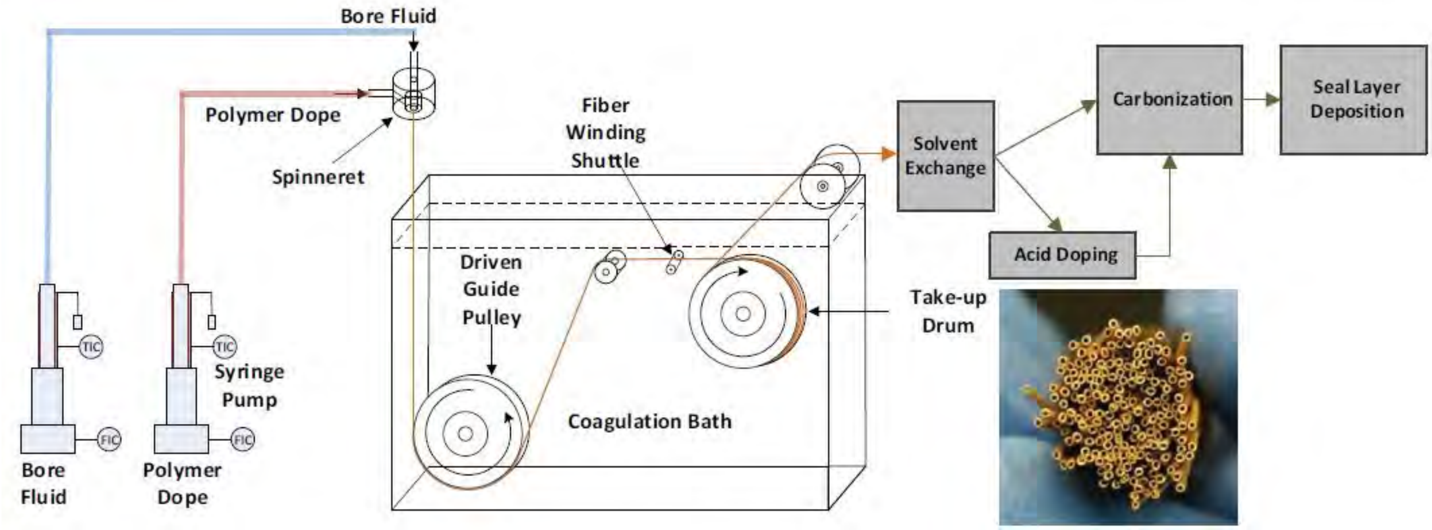

Figure 6: LANL lab-scale continuous hollow fiber spinning system.

SUNY manipulated the PBI-CMS HFM fabrication process to optimize HFM H_2/CO_2 separation performance. Figure 7a shows the H_2 permeance and H_2/CO_2 selectivity for a series of PBI-CMS HFMs fabricated under varied conditions. The project goal of 1,000 GPU H_2 permeance and H_2/CO_2 selectivity of 40 was definitively attained along the measured points under gas permeation testing at 250°C. Figure 7b shows the influence of temperature on the H_2/CO_2 separation performance of asymmetric PBI-CMS HFMs. The ideal H_2, CO_2, and N_2 permeance increases as the temperature increases from 150 to 300°C. The highest H_2 permeance of 1,090 GPU and H_2/CO_2 selectivity of 57 was measured at 300°C, which substantially exceeds the project goal.

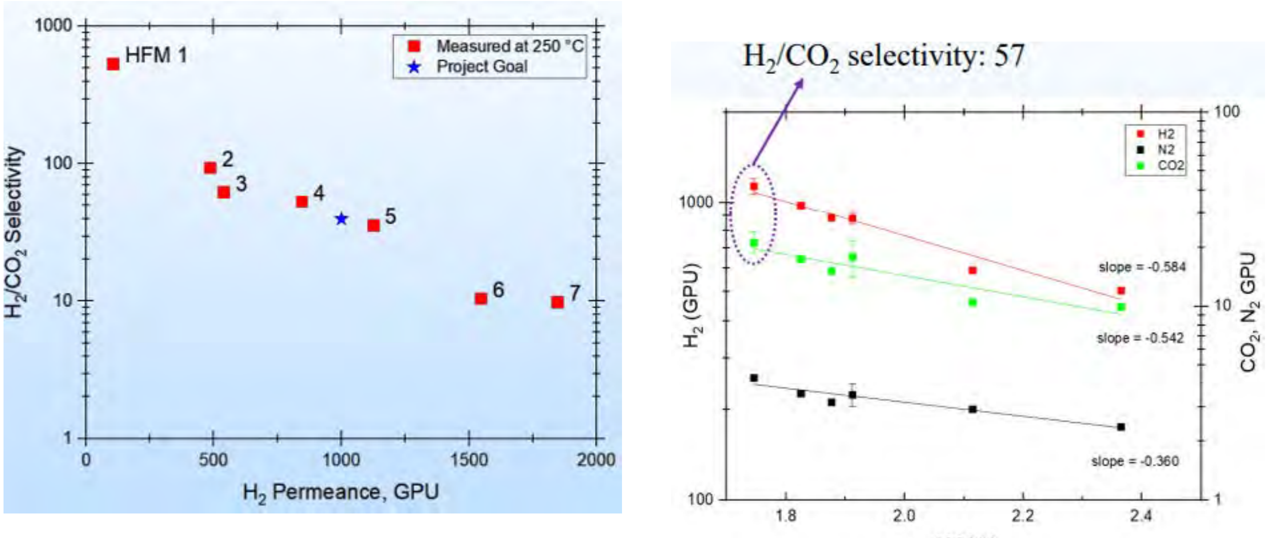

Figure 7a (left) and 7b (right): PBI-CMS HFM testing results.

Process implementation of CMS membrane modules would follow the basic flow diagram shown in Figure 8. Shifted syngas (1) containing mostly H_2 and CO_2 passes through membrane modules. Hydrogen selectively permeates and is swept away by N_2 (3), which is available in large quantities from the air separation unit producing oxygen for coal gasification (not shown on this figure). The H_2 and N_2 mixture comprises fuel gas (4) to be combusted in the power turbine. Retentate from the membrane modules is conditioned, dewatered, and compressed/pumped into liquid CO_2 for storage or use (2). With the CMS membranes able to withstand increased operating temperature of 200–300°C (as opposed to more conventional limit of 150°C), there is reduced cost of cooling syngas upstream of the membrane separation step, while improved permeability and selectivity afforded by the PBI-CMS HFMs reduces CO_2 processing costs downstream. These benefits combine to offer better economics for CO_2 capture than conventional approaches.

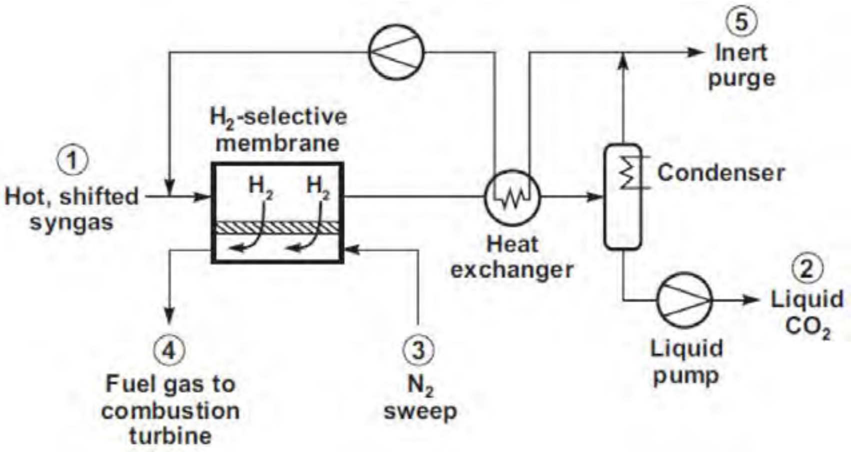

Figure 8: Membrane process integration in process cycle.

TABLE 1: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="3">Current R&D Value *</th><th colspan="3">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="3">carbonized acid-doped PBI</td><td colspan="3">carbonized acid-doped PBI</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="3">plain PBI</td><td colspan="3">plain PBI</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="3">0.2</td><td colspan="3">0.2</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="3">hollow fiber</td><td colspan="3">hollow fiber</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="3">20</td><td colspan="3">50</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>h</td><td colspan="3">120</td><td colspan="3">120</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m^2</td><td colspan="3">20</td><td colspan="3">20</td></tr>
<tr><td colspan="8">Membrane Performance</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">150</td><td colspan="3">200-300</td></tr>
<tr><td>CO_2 Pressure Normalized Flux</td><td>GPU or equivalent</td><td colspan="3">200</td><td colspan="3">1,000</td></tr>
<tr><td>CO_2/H_2O Selectivity</td><td>—</td><td colspan="3">0.5</td><td colspan="3">0.5</td></tr>
<tr><td>CO_2/H_2 Selectivity</td><td>—</td><td colspan="3">0.025</td><td colspan="3">0.017</td></tr>
<tr><td>CO_2/H_2S Selectivity</td><td>—</td><td colspan="3">2</td><td colspan="3">2</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="3">20</td><td colspan="3">20</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="3">mixed gas</td><td colspan="3">mixed gas</td></tr>
<tr><td colspan="8">Proposed Module Design</td></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="6">Countercurrent</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="6">~1,000</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="6">Permeate, CO_2-rich flow</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="6">~960,000</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">94.3</td><td colspan="2">43.6</td><td colspan="2">50.4</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">72.8</td><td colspan="2">41.9</td><td colspan="2">32</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="6">1/1</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{\text{kg/hr}}$</td><td colspan="6">~4.0</td></tr>
</table>

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Physical solution-diffusion.

Contaminant Resistance – Membranes are resistant to chemicals in the syngas.

Syngas Pretreatment Requirements – Removal of particles.

Membrane Replacement Requirements – Module lifetime is three to five years.

Waste Streams Generated – Water vapor will permeate with H_2, and the water stream will be produced after the H_2 combustion.

Proposed Module Design – See Figure 8. The pressure, temperature, and composition of the gas entering the membrane module are as follows:

		Composition						
Pressure	Temperature	vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
756	432	30.8	0.6	0.76	0.44	43.7	23.3	4700

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	43.01	—
Cost of Carbon Avoided	\$/tonne CO_2	60.74	—
Capital Expenditures	\$/MWhr	60.9[1]	60.9
Operating Expenditures	\$/MWhr	25.5/52.5[2]	52.5
Cost of Electricity	\$/MWhr	113.5/121.3[3]	—

[1] Capital Cost Factor*Total Overnight Capital/MWh-net

[2] without fuel / with fuel

[3] without transportation, storage and monitoring costs / with transportation, storage and monitoring costs

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Calculations Basis – The cost of Carbon Captured and Carbon Avoided in Table 2 are based on the supercritical, pulverized coal reference plant Case B12A, found in the “Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3” report (https://www.netl.doe.gov/energy-analysis/details?id=729). The Cost of Carbon Captured excludes the costs for transportation, storage, and monitoring. The Cost of Carbon Avoided includes the costs for transportation storage, and monitoring.

The costs for the current R&D case are based on Case B5B, found in the “Cost and Performance Baseline for Fossil Energy Plants Volume 1b: Bituminous Coal (IGCC) to Electricity Revision 2b – Year Dollar Update” report (https://www.netl.doe.gov/energy-analysis/details?id=1033).

Costs for the current R&D case and reference cases were adjusted to a cost basis of June 2011 US Dollars. Costs reported in Table 2 are in June 2011 US Dollars.

Scale of Validation of Technology Used in TEA – Laboratory scale experiments were conducted to assess the membrane technology performance. The TEA is a conceptual study on a full-scale power plant using the laboratory-measured performance metrics.

technology advantages

- The capability of CMS membranes with high permeance and selectivity to operate at high temperature eliminates the need for syngas cooling and avoids water vapor loss, which improves energy and cost efficiency of the carbon capture process.
- The simplicity of the membrane structure lowers its manufacturing cost.
- A membrane system does not contain moving parts or involve chemical reactions, conferring some operation and maintenance (O&M) advantages.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- Membrane capture systems (particularly those based on HFM modules) have compact footprint.

R&D challenges

- Assuring polymer performance and properties.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Durability and gas integrity of membrane modules (gas seals, fouling).
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

Many project activities are complete. However, evaluation of PBI-CMS HFMs in wet simulated syngas as a function of operating conditions and feed gas composition, study of membrane reactor-based WGS reaction, and techno-economic analysis (TEA) of the capture system in IGCC plant context continue.

available reports/technical papers/presentations

“Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties,” presented by Haiqing Lin and Leiqing Hu, University at

Buffalo, 2021 NETL Carbon Management Research Project Review Meeting, August 16, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Lin.pdf*

“Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties,” BP1 Project Review Meeting, March 27, 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10574&filename=+Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*

“Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties,” presentation by Haiqing Lin, SUNY Buffalo, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Carbon-Hollow-Fiber.pdf*

“Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties,” project kickoff meeting presentation, November 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=10570&filename=Development+of+Carbon+Molecular+Sieves+Hollow+Fiber+Membranes+Based+on+Polybenzimidazole+Doped+with+Polyprotic+Acids+with+Superior+H2%2fCO2+Separation+Properties.pdf*

“Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties,” presented by Haiqing Lin, State University of New York (SUNY) at Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-SUNY-Carbon-Molecular-Sieves.pdf*

“Unexpectedly Strong Size-Sieving Ability in Carbonized Polybenzimidazole for Membrane H_2/CO_2 Separation,” M. Omidvar, H. Nguyen, L. Huang, C.M. Doherty, A.J. Hill, C.M. Stafford, X. Feng, M.T. Swihart, and H. Lin, ACS Appl. Mater. & Interfaces, 11 (50), 47365-47372 (2019).

“Ultraselective Carbon Molecular Sieve Membranes with Unprecedented Performance for H_2/CO_2 Separation for Pre-combustion CO_2 Capture,” presented by Hien Nguyen, State University of New York (SUNY) at Buffalo, 2019 Materials Research Society, Boston, MA. December 2019.

Enabling Production of Low-Carbon Emissions Steel Through CO_2 Capture from Blast Furnace Gases (BFGs)

primary project goal

Dastur International Inc. (Dastur) is designing and engineering a solution to maximize decarbonization of available blast furnace gas (BFG) at Cleveland-Cliffs' 5-million-tonne/year integrated steel plant in Burns Harbor, Indiana. The project aims to capture 2.8 million tonnes per annum (mtpa) of carbon dioxide (CO_2) emissions from the BFG by designing and integrating a BFG flow distribution system and an innovative BFG conditioning process, and by deploying a proven solvent-based carbon capture technology. The overall process will capture more than 75% of CO_2 emissions from the available BFG at the cost of capture of around $42 per tonne of CO_2.

technical goals

- Design and engineer a cost-competitive, techno-economically viable, industrial-scale carbon capture system for Cleveland-Cliffs' Burns Harbor steel plant.
- Design and engineer a water-gas shift (WGS) unit to maximize CO_2 capture from a single point source and increase the CO_2 concentration at the carbon capture unit.
- Optimize the WGS-based gas conditioning and reforming system to convert and extract hydrogen (H_2)-rich fuel and syngas from the BFG for use in existing combustion and conversion to pure H_2 in the future.
- Evaluate and validate the downstream combustion operations of converted H_2-rich fuel using computational fluid dynamics (CFD) and operating models.
- Evaluate the best possible strategy for sourcing the required steam and electricity and optimize the amount of sourced inputs for the lowest overall cost of capture, as well as the cost of CO_2 avoided ($/tonne CO_2).
- Conduct a series of environmental and safety studies related to the project, namely solvent and CO_2 disposal/disposition studies, a wastewater treatment study, a permitting study and review, a hazard and operability (HAZOP) review, a constructability review, and an environmental health and safety (EH&S) risk assessment.
- Develop a techno-economic assessment (TEA) to determine the CO_2 capture costs.

technical content

Dastur is undertaking the initial engineering design of a scalable carbon capture system for BFG at Burns Harbor, without impacting the competitiveness and techno-economics of the steelmaking process. The envisaged project will also extract low-carbon, H_2-rich fuels from the BFG for enhanced usage within the steel plant downstream operations. The goal is to engineer and design an industrial-scale CO_2 capture solution to capture 95% of the CO_2 in the BFG consisting of H_2,

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Steel Blast Furnace Gas Conditioning Process

participant:
Dastur International Inc.

project number:
FE0031937

predecessor projects:
N/A

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Atanu Mukherjee
Dastur International Inc.
Atanu.M@dastur.com

partners:
Cleveland-Cliffs Inc.;
ION Clean Energy Inc.;
University of Texas at Austin

start date:
10.01.2020

percent complete:
40%

carbon monoxide (CO), and CO_2 before combustion, which equates to 75% of CO_2 emissions of the combusted BFG. This enables a competitive, environmentally friendly, and sustainable BFG-based process for producing low-carbon emissions steel.

The project proposes to capture 2.8 mtpa of CO_2 emissions from the available BFG at Burns Harbor by utilizing ION Clean Energy's solvent-based, state-of-the-art carbon capture technology, which has a proven carbon capture efficiency of more than 95%. To facilitate greater CO_2 capture, a compositional shift of the BFG is carried out using the WGS reactor. The initial engineering design system (Figure 1) uses a WGS compositional shift of the CO and water (H_2O) mixture in the BFG to raise the CO_2 concentration, resulting in better capture efficiency and maximizing the CO_2 at a single point source of carbon capture. The BFG is also enriched to an H_2-heavy fuel gas, with H_2 content of up to 36%.

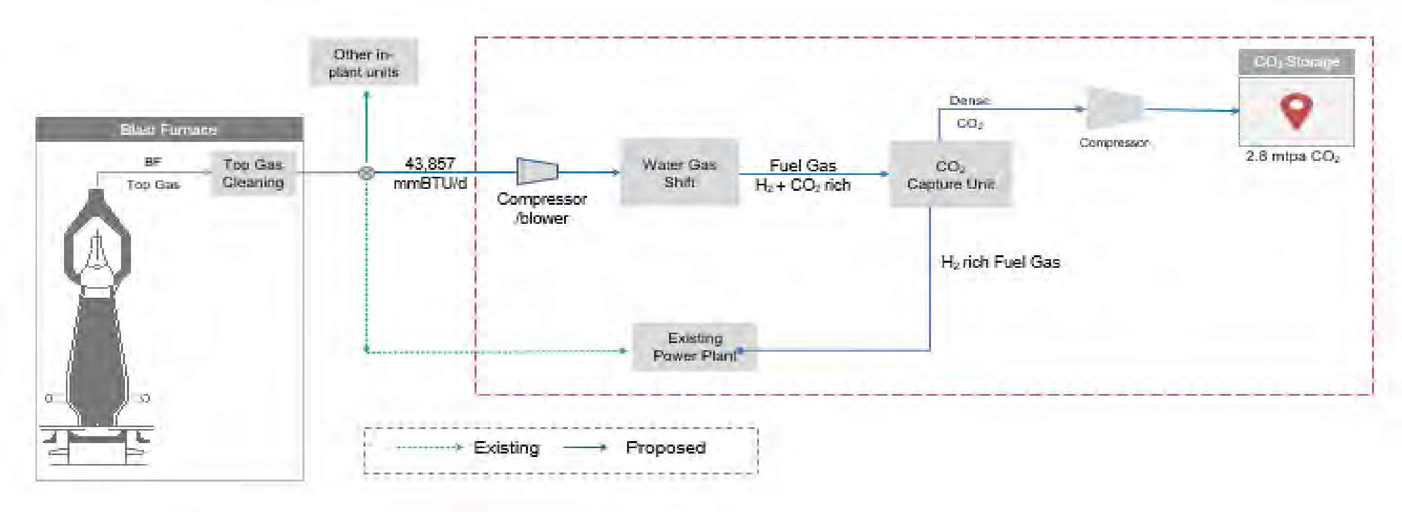

Figure 1: Flowchart of carbon capture system to be retrofitted to blast furnace.

Depending on the steam-to-dry-gas ratio required, external steam is added to perform the shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). Thereafter, the shifted gas from the WGS reactor is passed through the carbon Capture unit (CCU), which has a similar configuration to typical post-combustion amine-based CO_2 capture systems. In the CCU, the gas enters the absorber and interfaces with the carbon capture solvent, which absorbs the CO_2, leaving an H_2-rich gas. The solvent is routed to a stripper column where it is heated, releasing the captured CO_2. The captured CO_2 is compressed to pipeline pressure for transportation to locations for storage and/or utilization. The process parameters of the solvent are shown in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	80 – 150	100 – 150
Normal Boiling Point	°C	220 – 250	220 – 250
Normal Freezing Point	°C	< -15	< -20
Vapor Pressure @ 15°C	bar	<0.0001	<0.0001
Manufacturing Cost for Solvent	$/kg	-	-
Working Solution			
Concentration	kg/kg	0.65 – 0.80	0.65 – 0.80
Specific Gravity (15°C/15°C)	-	0.8 – 1.1	0.8 – 1.1
Specific Heat Capacity @ STP	kJ/kg-K	1.5 – 2.5	1.3 – 2.0
Viscosity @ STP	cP	<10	<10
Surface Tension @ STP	dyn/cm	<50	<50
Absorption			
Pressure	bar	1.0	1.0
Temperature	°C	40	40

Equilibrium CO_2 Loading	mol/mol	0.5 – 1.0	0.5 – 1.0
Heat of Absorption	kJ/mol CO_2	-1,600 to -1,750	-1,600 to -1,750
Solution Viscosity	cP	<20	<20
Desorption			
Pressure	bar	1.5 – 2.0	1.5 – 4.5
Temperature	°C	110 – 125	110 – 140
Equilibrium CO_2 Loading	mol/mol	0.05 – 0.20	0.05 – 0.20
Heat of Desorption	kJ/mol CO_2	<1,800	<1,800

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is the market price of chemical, if applicable; "Target" is the estimated manufacturing cost for new solvents or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – BFG is considered as input. Unless noted, BFG pressure, temperature, and composition received at project area (dry basis) should be assumed as:

		Composition							
Pressure	Temperature	vol%						ppmv	
psia	°F	CH_4	CO_2	H_2	N_2	CO	Ar	SO_X	NO_X
16.7	86	0.5	22	9	45	23	0.5	-	-

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

A number of power and steam-sourcing options are being investigated for this study. These include using a steam boiler, a combined heat and power system for supplementary power, and/or waste heat recovery (WHR) from coke-dry quenching at the coke oven plant. A summary of two such options being evaluated is provided in Figure 2.

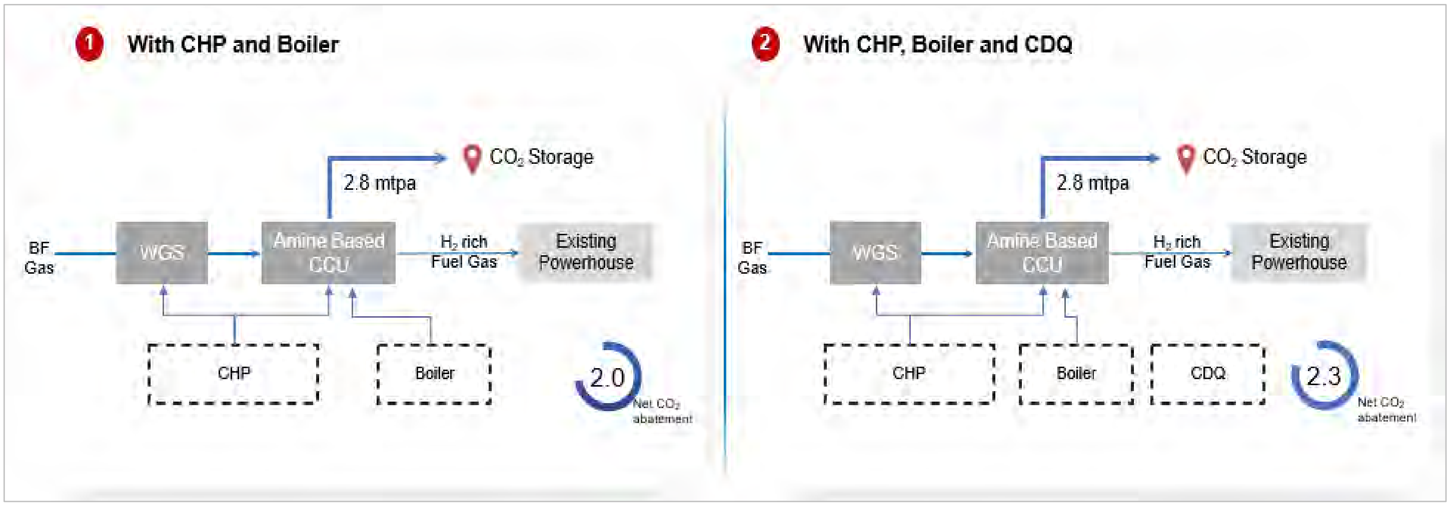

Figure 2: Steam and power-sourcing options.

The conditioned H_2-rich BFG has little to no CO_2. CFD models are being used to evaluate and validate the use of multiple H_2-rich combustion stream options in the firebox of the furnace under varying operating conditions and the performance in terms of temperature distribution, flame profiles, flashback, and nitrogen oxide (NO_X) formation. The performance of the conditioned H_2-rich BFG has been evaluated as a boiler fuel against the unconditioned BFG, using CFD modelling of combustion characteristics. The base case corresponds to the current boiler operations, wherein suitable amounts of BFG, coke oven gas, natural gas, and preheated air are injected into the boiler in a non-premixed fashion. The H_2-rich cases consist of H_2-rich gas replacing the BFG in the current fuel mix, with varying H_2 content, 32% and 36% by volume, corresponding to 77% and 100% CO shift in the WGS, respectively. The developed CFD model is validated against velocity, temperature, and gas composition data obtained during a typical boiler operation.

The simulation results for the base and the H_2-rich cases are compared for the degree of combustion from the exit gas composition, velocity and temperature profiles, wall heat flux profiles, and exit NO_X flow rate. It is observed that the H_2-rich gases behave largely similar to the BFG. This similarity stems from the proximity of the calorific value of these gases and is due to the fact that the H_2-rich gas has a moderate volume fraction of H_2 (32% and 36%). Moreover, the lack of pre-mixed combustion eliminates the possibility of flashbacks in all cases. Thus, it can be concluded that the H_2-rich gas can safely replace the BFG in the boiler without the need for any design modifications to the boiler. This also enables the shifting of BFG all the way up to 100% in the WGS and therefore maximizing the CO_2 capture volume, based on the requirements.

Finally, a TEA will be performed as a part of this study. Preliminary data at the onset of the project predicts an overall cost of capture of up to $42/tonne of CO_2 captured. This cost of capture excludes the cost of transportation and storage (e.g., 10 $/tonne).

technology advantages

- No oxidative degradation.
- Low volatile organic compound and nitrogen emissions.
- Increased maximum train size.
- Significantly smaller absorber and ducting.
- Outlet CO_2 is supercritical (possibility for high byproduct power production/energy recovery).

R&D challenges

- Implementation of heat-integration strategies.

- Verification of long-term solvent performance in the BFG environment.
- Selection of proper CO_2 storage location. More geological surveying is required.

status

The project has begun. The preliminary study has been performed and the plant location has been sited.

available reports/technical papers/presentations

Mukherjee, A. & Sarkar, A., 2021, “Enabling Production of Low Carbon Emissions Steel Through CO_2 Capture from Blast Furnace (BF) Gases (FE0031937).” Project Kickoff Meeting. Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=11014&filename=Enabling+Production+of+Low+Carbon+Emissions+Steel+through+CO2+Capture+from+Blast+Furnace+(BF)+Gases.pdf*.

Initial Engineering and Design for CO_2 Capture from Ethanol Facilities

primary project goal

The University of North Dakota Energy and Environmental Research Center (UNDEERC) and project partners Red Trail Energy LLC (RTE), Trimeric Corporation, and KLJ are completing an initial engineering design and cost estimate for the installation of a hybrid system for the capture and compression of carbon dioxide (CO_2) generated from an ethanol production facility near Richardton, North Dakota. The hybrid capture system combines commercially available technologies of chemical absorption to process the CO_2 emissions associated with heat production (i.e., steam generated by firing a natural gas boiler) and liquefaction to process the CO_2 emissions associated with bioprocessing at RTE's ethanol plant. The project team will complete a pre-front-end engineering and design (pre-FEED) analysis of the hybrid capture system, which includes an environmental health and safety (EH&S) risk assessment, a constructability review, identification of permits, and corporate approvals. A techno-economic assessment (TEA) and pre-FEED-level cost estimate will also be completed.

technical goals

- Design a hybrid capture system using CO_2 emissions from both bioprocessing and heat production at the host site facility.
- Complete a pre-FEED analysis of the hybrid capture system to include EH&S, a constructability report, identification of permits, and corporate approvals.
- Evaluation of performance and TEA in accordance with the U.S. Department of Energy's (DOE) methodology, as demonstrated by the bituminous baseline study.

technical content

The RTE carbon capture and storage (CCS) project is constructing a CO_2 capture facility adjacent to the RTE ethanol plant near Richardton (Figure 1), to ultimately inject about 180,000 tonnes of CO_2 annually more than a mile below RTE property for permanent storage. The hybrid capture system combines chemical absorption to capture and compress CO_2 emissions associated with heat production (i.e., natural gas steam boilers, ~130,000 tonnes/yr CO_2) and liquefaction to capture and compress CO_2 emissions associated with bioprocessing at the RTE operating ethanol facility (~180,000 tonnes/yr CO_2). The resulting 310,000 tonnes/yr CO_2 could then be destined for geologic injection and storage (Figure 2), or could be available for enhanced oil recovery (EOR) in the future because of the low oxygen (O_2) content of the CO_2 final product. This system was designed to use existing utilities to provide the required energy for potential hybrid capture operations. A conventional 30 wt.% monoethanolamine (MEA) absorber–stripper process was designed to capture the CO_2 from the boiler burner exhaust streams and to recover it as an essentially pure gas.

The liquefaction process was designed during the 2016–2017 study funded by DOE and the North Dakota Industrial Commission (NDIC) and conducted by the

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Hybrid Absorption-Liquefaction CO_2 Capture System for Ethanol Production Plants

participant:
University of North Dakota Energy and Environmental Research Center (UNDEERC)

project number:
FE0031938

predecessor projects:
N/A

NETL project manager:
Carl Laird
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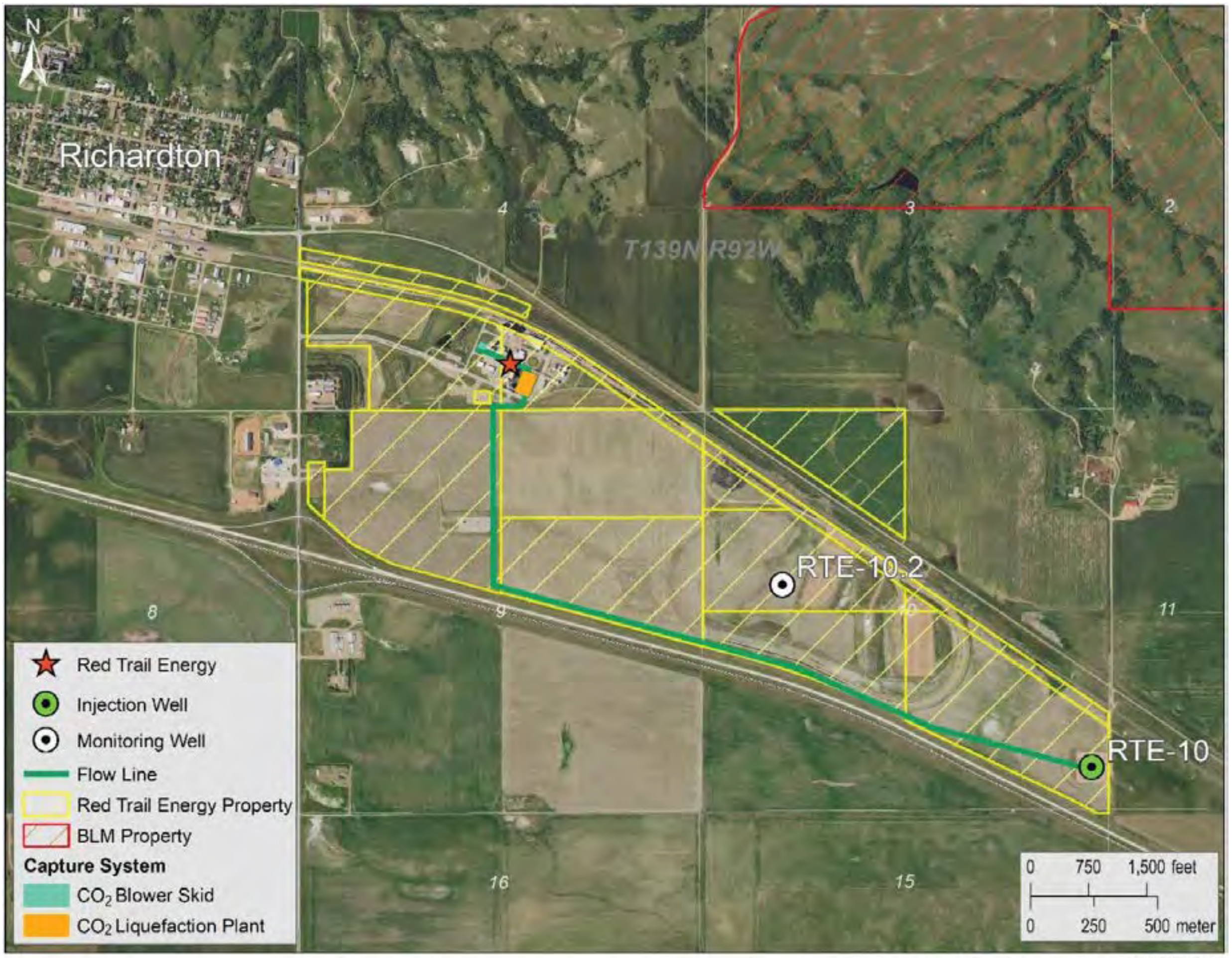
principal investigator:
Jason Laumb
University of North Dakota Energy and Environmental Research Center (UNDEERC)
jlaumb@undeerc.org

partners:
Red Trail Energy LLC; Trimeric Corporation

start date:
10.01.2020

percent complete:
89%

EERC and RTE to assess the overall technical feasibility to remove CO_2 and perform subsurface injection onsite. A more rigorous design was conducted by Trimeric Corporation in 2019.



EERC KL59582.AI

Figure 1: RTE ethanol facility and CCS site.

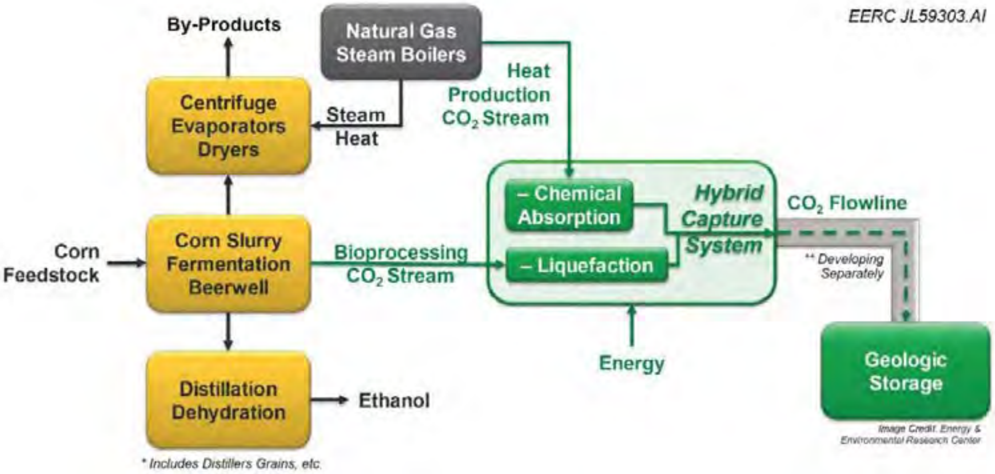


Figure 2: Block diagram of project process (*includes distillers' grains, etc.) at the RTE ethanol-CCS site; the hybrid capture system includes the required compression for geologic injection.

The hybrid capture system was designed to use RTE existing utilities to provide the required energy for potential operations. The liquefaction process captures the entirety of the nearly pure CO_2 (>99% dry) produced from RTE's fermentation process, compresses the CO_2 up to approximately 350 pounds per square inch gauge (psig), dehydrates the gas, and then liquefies it using a closed-loop ammonia refrigeration process. A conventional distillation column distills the liquid CO_2 to remove oxygen, in addition to other noncondensable gases. The chemical absorption process assumes 90% capture of the CO_2 from flue gas emitted by the two existing natural gas-fired boilers at the RTE facility, along with a potential new boiler, to provide the necessary steam for this portion of the hybrid capture process. The flue gas from the three boilers would contain a fraction of CO_2 (~4%) sufficient for capture and be fed to the absorption process, where CO_2 would be removed by employing MEA as a chemical solvent. The product CO_2 would be compressed and dehydrated, then combined with the CO_2 from the liquefaction process. The combined final CO_2 product stream could be then transported for geologic storage.

TABLE 1: SOLVENT PROCESS PARAMETERS*

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	68.0831	68.0831
Normal Boiling Point	°C	170.6	170.6
Normal Freezing Point	°C	10.4	10.4
Vapor Pressure @ 15°C	bar	<.001	<.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	0.3	0.3
Specific Gravity (15°C/15°C)	-	1.02	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.7	3.7
Viscosity @ STP	cP	2.5	2.5
Surface Tension @STP	dyn/cm	0.06	0.06
CO_2 Mass Transfer Rate [K_L]	m/s	—	—
CO_2 Reaction Rate	-	—	—
Thermal Conductivity	W/(m-K)	—	—
Absorption			
Pressure	bar	0	0
Temperature	°C	43	43
Equilibrium CO_2 Loading	mol/mol	2.1	2.1
Heat of Absorption	kJ/mol CO_2	1930	1930
Solution Viscosity	cP	1.8	1.8
Desorption			
Pressure	bar	0.7	0.7
Temperature	°C	115	115
Equilibrium CO_2 Loading	mol/mol	5.1	5.1
Heat of Desorption	kJ/mol CO_2	1930	1930

*Based on published commercial MEA data where available.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

CO_2 Mass Transfer Rate – Overall liquid phase mass transfer coefficient.

CO_2 Reaction Rate – A characterization of the CO_2 absorption trend with respect to time, as complete in the range of time as possible.

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Chemical/Physical Solvent Mechanism – Absorption/desorption process as expected for 30 wt.% MEA.

Solvent Contaminant Resistance – Solvent is sensitive to exposure to sulfur dioxide (SO_2), halogen, nitrogen oxide (NO_X), and trace metals.

Solvent Foaming Tendency – Foaming tendency considered low for this application.

Air Feed-Gas Pretreatment Requirements – Pretreatment is not required.

Solvent Make-Up Requirements – Process preliminary design includes "bleed and feed" process for solvent makeup/reclaiming at a projected rate of 0.44 tonnes/day. Reclaiming will be conducted offsite.

Waste Streams Generated – 30 wt.% MEA to be taken offsite for reclaiming.

Process Design Concept – See description above.

Proposed Module Design – Amine-based system is typical absorption/desorption system.

TABLE 2: HYBRID PROCESS CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	55	55
Capital Expenditures	\$/tonne CO_2	30	30
Operating Expenditures	\$/tonne CO_2	25	25

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per unit of CO_2 captured.

Calculations Basis – Calculations taken from fundamental quotes for standard commercially available items. Capital cost levels utilized from the National Energy Technology Laboratory (NETL) quality guidelines for cost estimation methodology.

Scale of Validation of Technology Used in TEA – This technology is based on existing equipment and processes. Novel techniques are not being employed.

Qualifying Information or Assumptions – Assumes 97% online factor, which matches operation time of the ethanol plant. Water, natural gas, and electricity costs based on current rates at the ethanol facility.

technology advantages

The 310,000 tonnes/yr CO_2 from the fermentation process and steam boilers within the RTE ethanol facility can be stored using this technology.

R&D challenges

Scale-up and variability of vendor estimates for operating costs of the supercritical carbon dioxide (sCO_2) loop process.

status

UNDEERC completed the pre-FEED design of a commercial-scale hybrid capture system. The TEA for the commercial-scale facility was also completed. Final reporting is currently being completed.

available reports/technical papers/presentations

Jason Laumb, "Initial Engineering and Design for CO_2 Capture from Ethanol Facilities," Project kickoff meeting presentation, Pittsburgh, PA, November 3, 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11016&filename=Initial+Engineering+and+Design+for+CO2+Capture+from+Ethanol+Facilities.pdf*.

Jason Laumb, "Initial Engineering and Design for CO_2 Capture from Ethanol Facilities," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Laumb.pdf*

Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant

primary project goal

Linde Inc., in partnership with Linde Engineering and BASF, is conducting an initial engineering design study (pre-front end engineering design [pre-FEED] equivalent) for a carbon dioxide (CO_2) capture plant based on Linde-BASF advanced aqueous amine-based OASE® blue technology installed at a Linde-owned, commercial-scale steam methane reforming (SMR) plant in the U.S. Gulf Coast. The plant is being designed to capture 95% of the CO_2 from a flue gas stream produced by the SMR (approximately 3,700 tonnes of CO_2 per day).

technical goals

- Complete an initial engineering design for the CO_2 capture plant, including the outside the battery limits (OSBL) equipment.
- Conduct a safety and environment analysis.
- Estimate total installed capital expense (CAPEX) and operating expense (OPEX).
- Conduct a techno-economic analysis (TEA) for CO_2 capture from the combustion flue gas of a commercial-scale SMR plant; develop accurate costs of CO_2 capture from SMR plants at the full commercial-scale.

technical content

The scope of the pre-FEED includes process units for pre-conditioning of the supply flue gas, the CO_2 capture plant island, the CO_2 compression train, the OSBL equipment, and any necessary components for connection to and integration with the SMR plant. The design employs Linde-BASF post-combustion CO_2 capture technology that utilizes BASF's aqueous amine-based OASE blue solvent. Linde-BASF's technology has been tested on both coal-fired and natural gas combined cycle (NGCC)-derived flue gas under a wide range of flue gas compositions and impurities, in which the solvent has exhibited favorable kinetics and reduced steam energy requirements, enhanced chemical and thermal stability compared to monoethanolamine (MEA) with greater resistance to oxygen and flue gas impurities, and a lower solvent circulation rate. In addition to the benefits the OASE blue solvent provides, the key Linde-BASF process features include: (1) high-capacity structured packing, enabling a reduced absorber diameter and capital costs; (2) regeneration of CO_2 at elevated pressure (up to 2.5 bara) that reduces downstream compression costs and compressor CAPEX, (3) optimized heat transfer in the rich/lean exchanger and heat recovery through use of the stripper interstage heater; and (4) a fast-response reboiler design. The basic process schematic is shown in Figure 1.

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Linde-BASF Amine Solvent-Based Technology Retrofit to SMR Plant

participant:
Linde Inc.

project number:
FE0031943

predecessor projects:
N/A

NETL project manager:
Mariah Richardson
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principal investigator:
Minish Shah
Linde Inc.
minish.shah@linde.com

partners:
Linde Engineering America;
Linde Engineering Dresden;
BASF

start date:
10.01.2020

percent complete:
85%

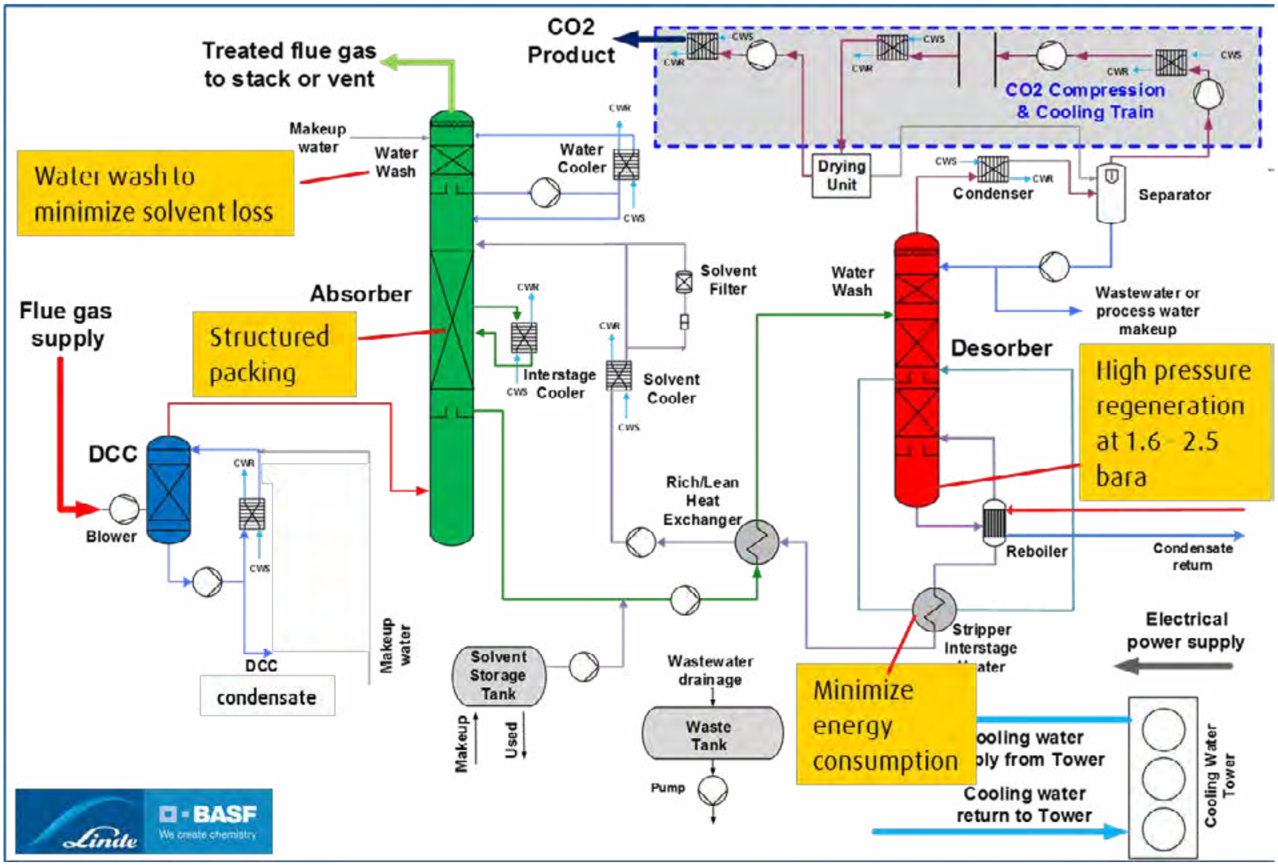

Figure 1: Process design with key features highlighted.

The plant concept involves a single-train design with one direct contact cooler (DCC), an amine unit with one absorber and one regenerator, and one CO_2 compression train (Figure 2).

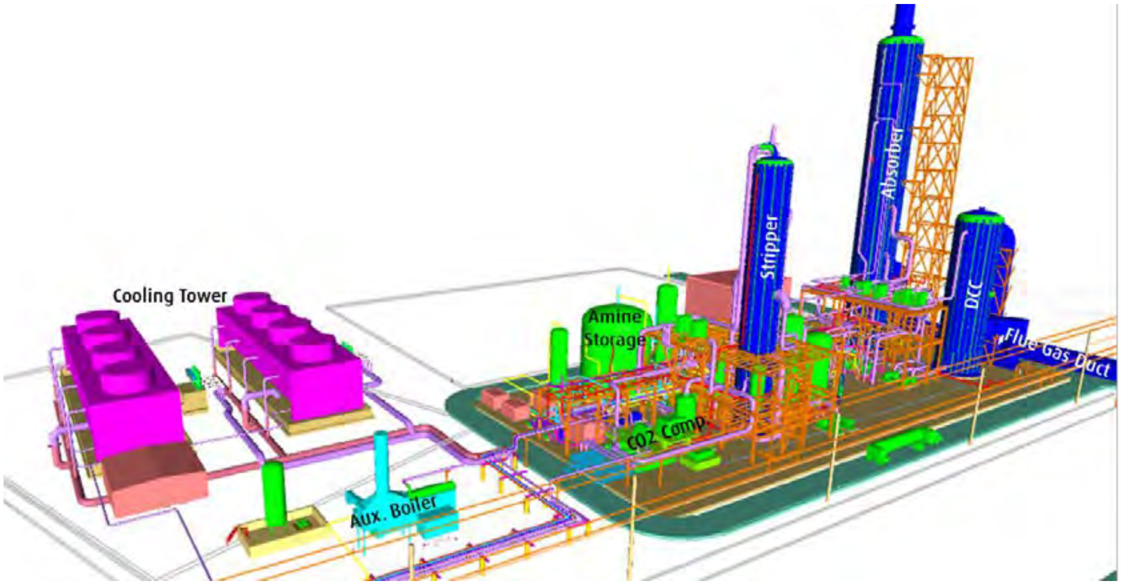

Figure 2: 3D layout of CO_2 capture plant.

The host site selected is one of the largest SMR plants in Linde's Gulf Coast fleet and is located in close proximity to saline aquifers and depleted oil and gas fields. Linde also owns and operates a large hydrogen (H_2) pipeline network and an H_2 storage cavern in the Gulf Coast.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	-5 to 25	-5 to 25
Vapor Pressure @ 15°C	bar	proprietary	proprietary
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15°C/15°C)	-	1.0–1.2	1.0–1.2
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	1.5–7.0	1.5–7.0
Absorption			
Pressure	bar	1.0	0.9–1.1
Temperature	°C	30–70	30–60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	—	—
Desorption			
Pressure	bar	1.6–2.5	1.6–2.5
Temperature	°C	proprietary	proprietary
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary	proprietary
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.22 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical H_2 plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 22% (dry basis). Therefore, the partial pressure of CO_2 is roughly 0.22 atm or 0.217 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition				
		vol%			ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**$N_2 + O_2 + Ar$**	**SO_x**	**NO_x**
14.7 psia	320°F	18.00	20.00	62.00	trace	trace

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – CO_2 in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – Anti-foaming injection is included in the design as a safeguard. During the previous pilot plant tests, foaming was not an issue.

Flue Gas Pretreatment Requirements – Any trace sulfur oxide (SO_X) must be kept below 5 ppm (by volume). Since SMR flue gas contains SO_X at much lower concentrations than 5 ppm, no pretreatment is required.

Solvent Make-Up Requirements – The OASE blue solvent make-up rate is determined by the sum of the amine losses from the absorber column, the stripper column, filtration unit, and amine reclaimer unit, and the rate of solvent degradation during operation over time. Low make-up rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from H_2 plants due to minimal aerosol.

Waste Streams Generated – Waste water from amine reclaimer unit will be sent to a treatment plant. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals.

Proposed Module Design – See Figure 1 for process configuration and Figure 2 for 3D layout. Single-train arrangement is used for large equipment, such as DCC, absorber, and stripper. Modularization is used where practical (e.g., pumps, heat exchangers, small vessels).

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	67	60
Cost of Carbon Avoided	\$/tonne CO_2	74	66
Capital Expenditures	\$/tonne CO_2	46	42
Operating Expenditures	\$/tonne CO_2	21	18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

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[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – Linde's proprietary method.

Scale of Validation of Technology Used in TEA – Technology Readiness Level (TRL) 6.

Qualifying Information or Assumptions – Project life—15 years; Natural Gas $3/MMBtu; Power $0.05/kWh; CO_2 transportation and storage costs excluded.

technology advantages

- The Linde-BASF partnership covers the entire value chain (solvent development and manufacturing; process technology; engineering, procurement, and construction [EPC]; and operations).
- The SMR host site offers favorable access to geological storage or use in enhanced oil recovery with low CO_2 injection costs.
- Higher CO_2 content in SMR flue gas (~20 vol% dry basis) compared to coal- and natural gas-fired flue gases enables a smaller absorber diameter needed to achieve greater than 95% capture at ambient pressure, leading to lower CAPEX.
- Aerosol concentrations in SMR flue gas stream are much lower than in coal or NGCC flue gas streams.
- The CO_2 produced by the Linde-BASF post-combustion capture plant will contain greater than 99.9 mol% (dry) CO_2 and to as low as 10 parts per million by volume (ppmv) oxygen (O_2).

R&D challenges

- Technology integration with operations at the SMR plant.
- CAPEX for transportation and site installation of large size equipment and piping.

status

The initial engineering design study, the safety and environmental analysis, and the CAPEX estimate for the entire CO_2 capture plant have been completed. The OPEX estimate and TEA are underway.

available reports/technical papers/presentations

M. Shah, "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant" presented at the Carbon Management and Natural Gas & Oil Research Project Review Meeting, Virtual Session – Integrated CCUS Projects and FEED Studies, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Shah.pdf*.

M. Shah, et.al., "Engineering Design of a Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant" Kickoff meeting presentation, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11025&filename=Engineering+Design+of+a+Linde+BASF+Advanced+Post+Combustion+CO2+Capture+Technology+at+a+Linde+Steam+Methane+Reforming+H2+Plant.pdf*

Initial Engineering Design Study for Advanced CO_2 Capture from Hydrogen Production Unit at Phillips 66 Rodeo Refinery

primary project goal

Phillips 66, with the assistance of Worley Group Inc., is performing an initial design of a commercial-scale, advanced carbon capture and storage (CCS) system that separates and stores approximately 190,000 tonnes per year net carbon dioxide (CO_2) with 90%+ carbon capture efficiency from an existing steam methane reforming (SMR) plant at the Phillips 66 Rodeo Refinery. The project goal is to analyze the technical results of three different carbon capture configurations and then select the one with the smallest predicted impact to the average levelized cost of hydrogen and produce an advanced engineering design for a commercial-scale unit based on the selected configuration.

technical goals

- Evaluate several proposed solvents for use in an absorption cycle and assess the performance of each, selecting one to utilize.
- Design and evaluate three different carbon capture configurations using a preliminary TEA. Select the best option for minimum cost of hydrogen production.
- Design and create an initial engineering package for the selected solvent and configuration.
- Perform a final TEA on the complete system.
- Perform an environmental health and safety (EH&S) analysis.

technical content

Phillips 66, in collaboration with the Worley Group Inc., is designing a commercial-scale carbon capture unit that could be installed onto the Phillips 66 Rodeo Refinery's SMR plant. The unit would capture 90% of the CO_2 produced by the plant. The first part of the project consists of a qualitative review of different commercially available technology providers' design packages. One licenser will then be chosen to proceed forward with the proposed three different carbon capture configurations.

The next phase of the project is focused on applying the selected technology to three separate CO_2 capture configurations: (1) capture from SMR flue gas and from the pressure-swing adsorption (PSA) tail gas; (2) capture from syngas before the PSA and from the SMR flue gas; and (3) capture from SMR flue gas only (post-combustion). By performing a TEA comparing these three options, the highest-ranked CCS system configuration with the lowest impact to the levelized cost of hydrogen will be selected. Consideration will also be given to the project's capital cost estimate, ease of integration into the existing refinery, solvent cost and stability, and the expected reliability of the new systems. The study team will

program area:
Point Source Carbon Capture

ending scale:
pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Solvents

project focus:
Solvent-Based Post-Combustion Carbon Capture System for NG Reforming

participant:
Phillips 66

project number:
FE0032109

predecessor projects:
N/A

NETL project manager:
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principal investigator:
Robert Henderson
Phillips 66
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partners:
Worley Group Inc.

start date:
03.01.2022

percent complete:
5%

further advance engineering efforts for completing the initial engineering design for the selected CCS configuration, such that the next phase of engineering can proceed.

After selecting the most viable option, engineering will proceed and an initial engineering design package of the chosen system will be created, including process flow diagrams (PFDs), piping and instrumentation diagrams (P&IDs), heat and mass balances, and equipment datasheets. Finally, a TEA will be completed as a part of this study.

TABLE 1: INDUSTRIAL PLANT CARBON CAPTURE

Economic Values	Units	Calculated Project Value
Cost of Carbon Captured	\$/tonne CO_2	TBD
Cost of Carbon Avoided	\$/tonne CO_2	TBD
Capital Expenditures	\$/tonne CO_2	TBD
Operating Expenditures	\$/tonne CO_2	TBD

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue stack (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
Psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	425	18.0	18.3	61.4	1.5	0.7	5	10

technology advantages to be considered

- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.
- Environmentally benign (i.e., low parasitic load, near-zero emissions, and negligible solvent makeup).
- Low thermal and oxidative degradation rates result in good solvent stability, reducing solvent makeup rates and associated operating costs (OPEX).
- Low specific reboiler duty and solvent stability result in smaller capture plant equipment, reducing capital expenditure (CAPEX).

R&D challenges

- Implementation of heat-integration strategies.
- Verification of long-term solvent performance in natural gas-fired flue gas environment.

status

Project has started. Technology provider contact has been initiated.

available reports/technical papers/presentations

N/A.

LafargeHolcim CO_2MENT Colorado Project

primary project goal

Electricore Inc. is a consortium of both public and private entities working to accelerate the implementation of carbon capture technology at a cement production site in Florence, Colorado. The CO_2MENT project facility is owned and operated by LafargeHolcim, which will implement Svante's VeloxoTherm™ adsorption technology in a first-of-a-kind (FOAK) commercial-scale carbon capture facility designed by Kiewit Engineering Group Inc., slated to capture more than 1.5 million tonnes of carbon dioxide (CO_2) per year.

technical goals

- Complete feasibility studies (FEL-1 and FEL-2) to estimate facility performance and project execution strategy.
- Complete a hazard and operability (HAZOP) analysis to assess project risks and develop a risk management plan.
- Perform an energy cost optimization study and a complete techno-economic analysis (TEA).
- Complete a pre-front-end engineering design (pre-FEED) study.
- Complete the overall project execution strategy of carbon capture facility and surrounding infrastructure (pipeline connections, storage site facilities, renewable, etc.).

technical content

The VeloxoTherm process developed by Svante is comprised of a rapid-cycle temperature swing adsorption (RC-TSA) process that uses a patented architecture of structured adsorbent beds (SABs) and a novel process design and embodiment to capture CO_2 from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties that serve to greatly improve the performance of gas separation, enabling fast cycle times and small equipment sizes that deliver attractive capture economics. Figure 1 shows the commercial-scale rotary adsorption machine (RAM) design at the core of the technology. Svante uses metal organic framework (MOF) solid adsorbents that have very high surface-to-volume ratios, instead of liquid chemicals (amines or potassium hydroxide), to capture CO_2. This new class of advanced sorbent materials, MOF CALF-20, has been developed by Svante and lab-tested under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FE0031732 and field-tested in Q3-2020 at a LafargeHolcim cement plant in Vancouver, Canada. The material will also be used in Q3-2022 at an engineering-scale demonstration plant of about 25 tonnes per day (TPD) using natural gas post-combustion flue gases in Chevron's Kern River, California, under DOE Cooperative Agreement No. DE-FE0031944.

The VeloxoTherm adsorption system is planned for use at LafargeHolcim's portland cement plant in Florence, Colorado. This location is beneficial, as it is near several ideal CO_2 storage locations, including a local saline aquifer and the Sheep Mountain natural CO_2 reservoir.

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Sorbents

project focus:
Rapid-Cycle Temperature-Swing Adsorption Process at Cement Plant

participant:
Electricore Inc.

project number:
FE0031942

predecessor projects:
N/A

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partners:
Svante Inc.; Kiewit Engineering Group; LafargeHolcim; Oxy Low Carbon Ventures; Total S.A.

start date:
11.09.2020

percent complete:
90%

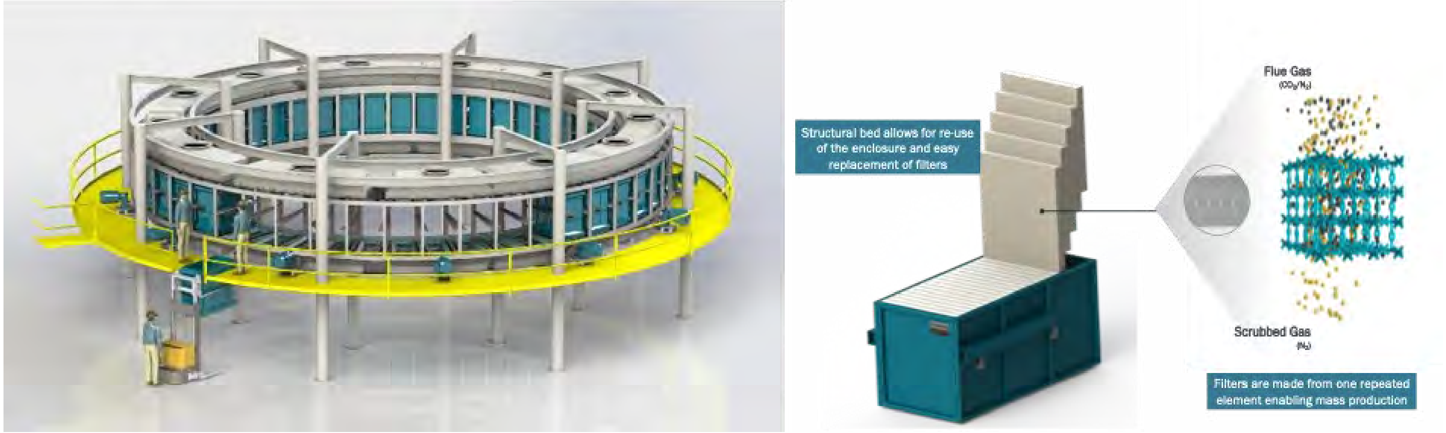

Figure 1: Svante VeloxoTherm™ commercial-scale rotary adsorption machine.

The MOF CALF-20 sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. The sorbent process parameters used for the FEL-1 and FEL-2 design studies are reported in Table1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	350-380	350-380
Bulk Density	kg/m^3	NA	NA
Average Particle Diameter	mm	0.31-0.35	0.31-0.35
Particle Void Fraction	m^3/m^3	NA	NA
Packing Density	m^2/m^3	2300-2500	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Thermal Conductivity	W/(m-K)	0.25-0.35	0.25-0.35
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	50	50
Equilibrium Loading (20% CO_2)	g mol CO_2/kg	1.7-1.9	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			
Pressure	bar	0.8-1.0	0.8-1.0
Temperature	°C	120-140	120-140
Equilibrium CO_2 Loading (20% CO2)	g mol CO_2/kg	0.3-0.4	0.3-0.4
Heat of Desorption	kJ/mol CO_2	35-38	35-38
Proposed Module Design			
Flow Arrangement/Operation	—	Rapid cycle rotary valves moving bed	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95 95	150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry sorbent measured with 20% CO_2 in nitrogen (N_2) mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 parts per million (ppm) SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional Direct Contact Cooler (DCC).

Sorbent Make-Up Requirements – Three- to five-year lifetime without bed replacement.

Waste Streams Generated – No chemicals in depleted N_2 and typical cooling water blow-down.

The planned plant will utilize a solar energy and battery storage system power purchase agreement to provide supplemental energy to the plant, ensuring smooth operation without interruption during hours of high demand.

By completing the feasibility engineering study (FEL-2) for a fit-for-purpose design at the LafargeHolcim cement plant, this technology represents a significant step forward for large-scale deployment of carbon capture and storage. Given the near-term potential for increased 45Q tax credit pricing to $85/tonne and voluntary emissions credits, the business analysis pointed to significant potential realizable economic value for the project, as shown in Table 2.

TABLE 2: CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	50	30
Cost of Carbon Avoided	\$/tonne CO_2	Site specific	Site specific
Capital Expenditures	\$/TPD	70,000-80,000	60,000-70,000
Operating Expenditures	\$/tonnes CO_2	26-28	20-23
Cost of Electricity	\$/tonnes CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity for the capture unit.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5–6 cents per kWh.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the TEA from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs of the capture unit compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).
- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.

R&D challenges

- Technology scaling of filter manufacturing to commercial scale.
- Technology scaling of RAM to commercial-scale.
- Cost and schedule uncertainties of project execution.
- Access to water, carbon-free electricity, and storage options.

status

All work for Budget Period 1 is nearing completion. The key finding was that significant work will be required during the next phase (FEED Study and Execution) to better define commercial and financial terms of the electricity and natural gas supplies and CO_2 storage, which will be critical for the successful Financial Investment Decision (FID) of this project.

available reports/technical papers/presentations

Electricore, Inc., 2020, "LH CO_2MENT Colorado Project." Project Kickoff Meeting. U.S. Department of Energy: National Energy Technology Laboratory (DOE/NETL). FE0031942. Pittsburgh, PA. November 9, 2020. *https://netl.doe.gov/projects/plp-download.aspx?id=11020&filename=LH+CO2MENT+Colorado+Project.pdf*.

Letourneau, C. & Jelen, D., "LafargeHolcim CO_2MENT Colorado Project." 2021 NETL Carbon Management and Oil & Gas Research Project Review Meeting. Pittsburgh, PA. August 3, 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Jelen.pdf*

Engineering Study of Svante's Solid Sorbent Post-Combustion CO_2 Capture Technology at a Linde Steam Methane Reforming H_2 Plant

primary project goal

Linde Inc., in coordination with Linde Engineering Americas, Linde Engineering Dresden, and Svante Inc., is conducting an initial engineering design of a commercial-scale carbon capture plant utilizing the Svante VeloxoTherm™ solid adsorbent carbon dioxide (CO_2) capture technology installed at an existing Linde-owned steam methane reforming (SMR) hydrogen (H_2) production plant in Port Arthur, Texas. The overall system is being designed to capture approximately 1,000,000 tonnes/year net CO_2 with at least 90% carbon capture efficiency while producing "blue" H_2 with 99.97% purity from natural gas.

technical goals

- Develop an initial engineering design and overall process design package for the CO_2 capture process integrated with the H_2 production facility.
- Prepare a capital cost estimate, including the cost of capture in \$/tonne CO_2 net captured from the H_2 plant, and the levelized cost of hydrogen.
- Generate a commercial-scale TEA of this post-combustion capture technology.
- Complete a Technology Maturation Plan (TMP) and Environment, Health, and Safety (EH&S) Risk Assessment.

technical content

The VeloxoTherm process developed by Svante is comprised of a rapid cycle thermal swing adsorption (TSA) process that uses a patented architecture of structured adsorbent beds (SABs) and a novel process design and embodiment to capture CO_2 from industrial and natural gas-fired flue gas streams. SABs possess unique physical and transport properties, which serve to greatly improve the performance of gas separation, enabling fast cycle times and small equipment sizes that deliver attractive capture economics. Figure 1 shows the rotary adsorption machine (RAM) design at the core of the technology. Svante uses solid adsorbents that have very high surface-to-volume ratios, instead of liquid chemicals (amines or potassium hydroxide), to capture CO_2. A new class of advanced sorbent materials, metal organic framework (MOF)-based sorbent material (CALF-20), has been developed by Svante and lab-tested under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FE0031732, and is being field-tested (since January 2021) at a cement plant in Vancouver, Canada.

program area:

Point Source Carbon Capture

ending scale:

pre-FEED

application:

Post-Combustion Industrial PSC

key technology:

Sorbents

project focus:

Svante VeloxoTherm™ CO_2 Capture Technology Applied to SMR Plant

participant:

Linde Inc.

project number:

FE0032113

predecessor projects:

N/A

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partners:

Linde Engineering Americas; Linde Engineering; Dresden GmbH; Svante Inc.

start date:

10.01.2021

percent complete:

17%

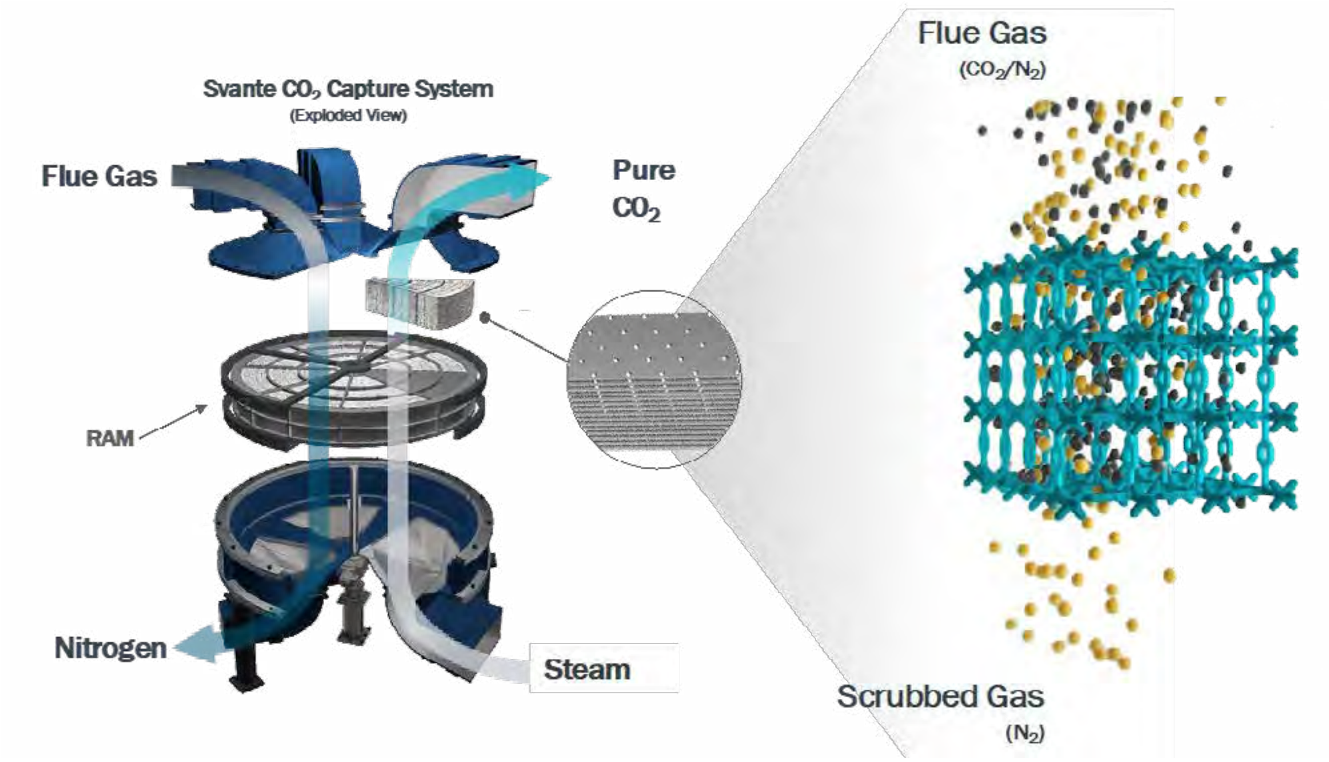

Figure 1: VeloxoTherm™ rotary adsorption machine.

This sorbent material exhibits unique resistance to sulfur oxide (SO_X), nitrogen oxide (NO_X), and oxygen impurities, as well as moisture swing. The VeloxoTherm process has been scaled-up to 30 TPD of CO_2 and is undergoing demonstration with flue gas derived from natural gas combustion at Cenovus in Canada using a first-generation sorbent material of amine-doped silica. In this project, the team plans to leverage the design and learnings from the Cenovus 30 TPD project to improve the performance and flexibility of a second-of-a-kind (SOAK) engineering-scale plant (400 Series) using CALF-20 MOF sorbent material.

The project team is developing an engineering design package comprised of the core technology; process units inside the battery limits (ISBL) of the CO_2 capture unit, such as flue gas conditioning and CO_2 product purification; and balance of plant components outside the battery limits (OSBL) of the capture plant.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
Weight/Bed Volume	kg/m^3	350-380	350-380
Bulk Density	kg/m^3	N/A	N/A
Adsorbent Particle Diameter	mm	0.31-0.35	0.31-0.35
Particle Void Fraction	m^3/m^3	N/A	N/A
Wetted sheet area/bed volume	m^2/m^3	2300-2500	2300-2500
Solid Heat Capacity @ STP	kJ/kg-K	1.4-1.6	1.4-1.6
Thermal Conductivity	W/m°K	0.25-0.35	0.25-0.35
Manufacturing Cost for Sorbent	$/kg	30-35	20-25
Adsorption			
Pressure	Bar (a)	1–1.1	1–1.1
Temperature	°C	50	50
Equilibrium Loading – 20% CO_2	g mol CO_2/kg	1.7-1.9	1.7-1.9
Heat of Adsorption	kJ/mol CO_2	35-38	35-38
Desorption			

Pressure	Bar(a)	0.8-1.0		0.8-1.0
Temperature	°C	120-140		120-140
Equilibrium CO_2 Loading	g mol CO_2/kg	0.3-0.4		0.3-0.4
Heat of Desorption	kJ/mol CO_2	35-38		35-38
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation			Rapid Cycle rotary valve moving bed	
Flue Gas Flowrate	kg/hr		596,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90-95	95	150

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the laminated sorbent composite sheet area/filter bed volume.

Equilibrium Loading – The basis for CO_2 loadings is mass of dry, sorbent measured with 20% CO_2 in N_2 mixture without moisture.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High oxidation resistance below 50 ppm SO_X and NO_X.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable under direct steam regeneration.

Flue Gas Pretreatment Requirements – Conventional direct contact cooler.

Sorbent Make-Up Requirements – Three- to five-year year lifetime without bed replacement.

Waste Streams Generated – No chemicals in VeloxoTherm exhaust gas, water treatment system blowdown.

Process Design Concept – Flowsheet/block flow diagram shown in Figure 2.

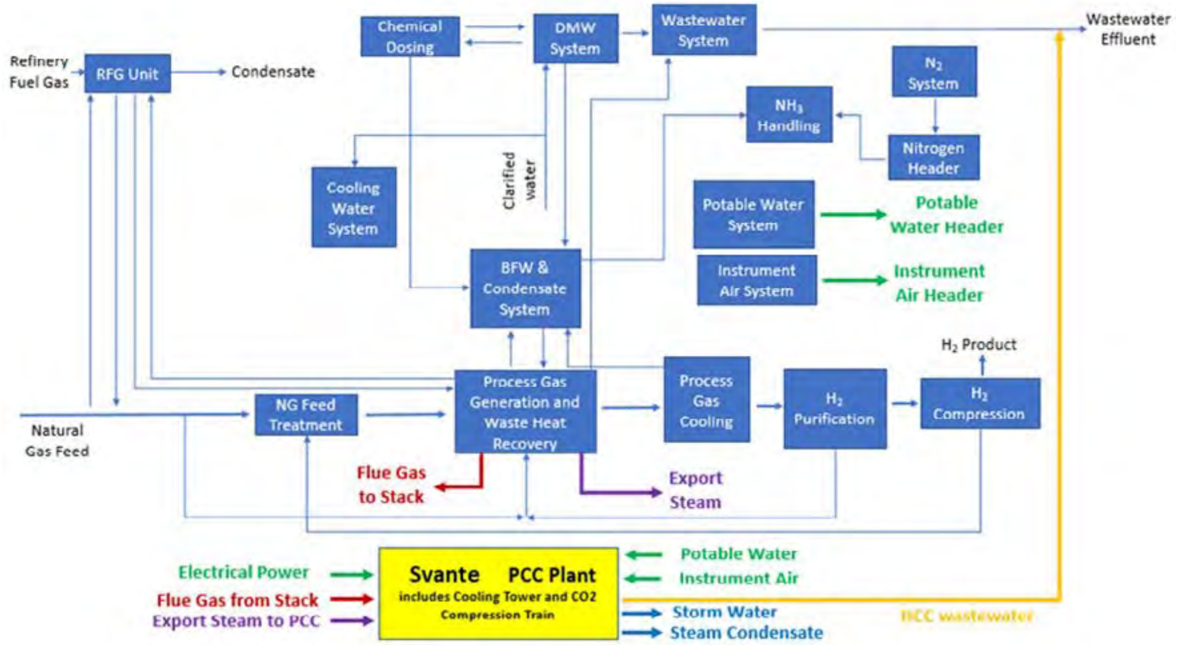

Figure 2: Flowsheet/block flow diagram of process.

TABLE 2: POWER PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	50	30
Cost of Carbon Avoided	$/tonne CO_2	Site specific	Site specific
Capital Expenditures	$/TPD	70,000-80,000	60,000 to 70,000
Operating Expenditures	$/tonne CO_2	26-28	20-23
Cost of Electricity	$/ tonne CO_2	12-18	12-18

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided is site specific depending on the source of electricity and steam.

Capital Expenditures – Projected capital expenditures in dollars per tonne per day of capacity.

Operating Expenditures – Projected operating expenditures in dollars per unit of tonne of CO_2 produced including filter bed replacement and compression cost.

Cost of Electricity – Projected cost of electricity per unit of tonne of CO_2 produced for a range of price of electricity of 3.5 to 6 cents per kwh.

Scale of Validation of Technology Used in TEA – The technology numbers were validated for use in the preliminary TEA from pilot-scale data.

technology advantages

- Svante's technology has the potential to enable a 50% reduction in capital costs compared to first-generation approaches.
- Novel technology replaces large chemical solvent towers (conventional approach) with a single piece of compact equipment, significantly reducing capital expenses (CAPEX).

- Advanced sorbent material exhibits sharper temperature and pressure swing absorption and desorption, which allows for lower energy loads and faster kinetic rates.
- The proprietary material also exhibits unique resistance to SO_X and NO_X, oxygen impurities, and moisture swings.

R&D challenges

- Integration with operations at the SMR plant.
- Engineering-scale testing and analysis

status

Linde Inc. has completed their preliminary basis of design and process design package. The technology design and engineering efforts are currently underway.

available reports/technical papers/presentations

Nicki Stuckert, Bill Chesser – "SMR CO_2 Capture Engineering Study." Project kickoff meeting presentation [WebEx meeting] October 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11229&filename=Engineering+Study+of+Svante%27s+Solid+Sorbent+Post-Combustion+CO2+Capture+Technology+at+a+Linde+Steam+Methane+Reforming+H2+Plant.pdf.*

Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant

primary project goal

Membrane Technology and Research Inc. (MTR), partnered with Sargent & Lundy (S&L) and CEMEX, is performing an initial engineering design of a full-scale Polaris membrane carbon dioxide (CO_2) capture system (approximately 1 million metric tonnes of CO_2 per day) applied to the CEMEX Balcones cement plant located in New Braunfels, Texas. This study will produce estimates of the cost and performance of a first-of-its-kind industrial membrane capture plant at a cement plant. The technical activities include completing a project design basis and process design; estimating the cost of the capture plant construction and installation; performing an environmental health and safety (EH&S) review, permitting and constructability reviews, and a hazard and operability study (HAZOP); and preparing a techno-economic analysis (TEA). S&L, an engineering, procurement and construction management contractor, will have the lead role in conducting the design study. CEMEX is the owner and operator of the cement plant and will provide plant-specific information on the Balcones facility for this study.

technical goals

- Complete an initial engineering design of the MTR membrane CO_2 capture process applied to the CEMEX Balcones cement plant located in New Braunfels, Texas.
- Complete a detailed engineering study for the membrane capture plant, including the process design with appropriate engineering drawings, system cost, constructability plan, and project execution schedule.
- Complete a TEA and Technology Maturation Plan (TMP) for the membrane capture system at the cement plant prepared per U.S. Department of Energy (DOE) guidelines.
- Complete an EH&S risk assessment and an environmental and permit review for the CEMEX host site.

technical content

MTR has developed a composite membrane called Polaris that sets the standard for post-combustion capture membranes. With an average CO_2 permeance of 1,000 gas permeation units (GPU) and a CO_2/N_2 pure-gas selectivity of 50, Polaris was a step-change improvement over typical commercial CO_2-selective membranes used for natural gas treatment. This improvement is illustrated in Figure 1, where membrane performance is compared in the form of a trade-off plot of CO_2/N_2 selectivity versus CO_2 permeance. Better membranes will have properties that move up and to the right on this plot.

In addition to showcasing the benefits of Polaris over conventional membranes, Figure 1 also shows some of the more recent improvements in the performance of Polaris membranes. A second-generation (Gen-2) version of the membrane has been scaled-up to pilot production, and an advanced Polaris membrane has been

program area:
Point Source Carbon Capture

ending scale:
Pre-FEED

application:
Post-Combustion Industrial PSC

key technology:
Membranes

project focus:
Membrane Technology for Cement Plant

participant:
Membrane Technology and Research Inc.

project number:
FE0031949

predecessor projects:
N/A

NETL project manager:
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partners:
CEMEX Inc.; Sargent & Lundy

start date:
10.01.2020

percent complete:
88%

produced at the lab scale. These developments demonstrate that the Polaris membrane technology continues to improve.

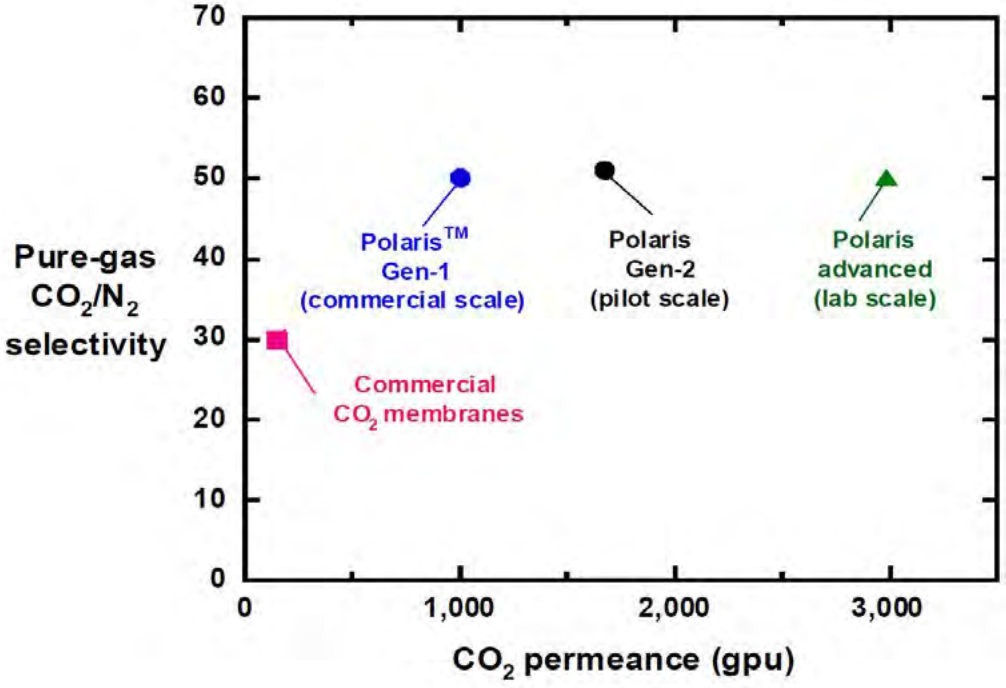

Figure 1: A CO_2/N_2 trade-off plot showing data for several generations of MTR Polaris, compared with the properties of the standard commercial natural gas membrane. Data are pure-gas values at room temperature.

The Gen-1 Polaris membranes were initially validated in field testing at the National Carbon Capture Center (NCCC), and are now being used in commercial natural gas and refinery membrane applications. The Gen-2 Polaris membrane has also been tested at the NCCC, and will be used on an upcoming engineering-scale field test at the Technology Centre Mongstad (TCM) in Norway (under DE-FE0031591).

As part of earlier MTR development programs, a low-pressure-drop membrane module specifically designed for a flue gas CO_2 capture process was created. Figure 2a shows a photo of a prototype of this planar module during testing at the NCCC. The simple straight-flow path of the new module results in a pressure-drop that is four-times lower than that measured for a conventional spiral-wound module (Figure 2b). This reduced pressure drop represents savings in fan power, equivalent to about 20–25 kWe/tonne of CO_2 capture. In addition to testing at the NCCC, the performance benefits of the planar module were verified in testing at Babcock & Wilcox and the University of Texas at Austin in separate DOE programs.

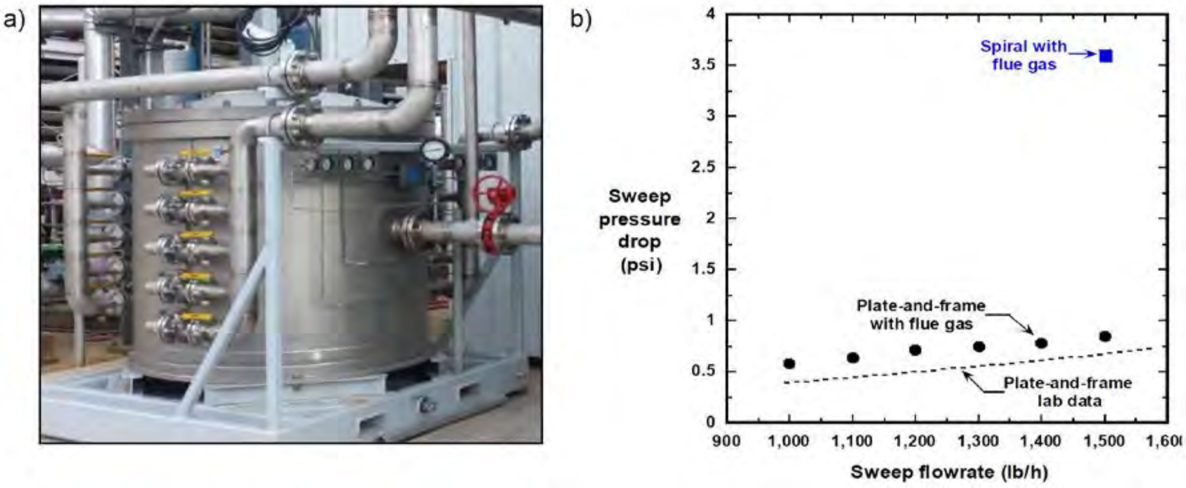

Figure 2: (a) Photo of the prototype planar module during testing at the NCCC, and (b) measured pressure drop in the module, compared to a conventional spiral-wound module.

The prototype planar module shown in Figure 2 was built in a local shop with machined parts and a stainless steel pressure vessel, resulting in relatively high costs. With the concept proven, the project team has transitioned to a lower-cost design based on reusable aluminum or single-use injection-molded, fiber-reinforced thermoplastics to form a stackable membrane module complete with integrated internal gas distribution. These low-cost modules are being used at the TCM field test in Norway. The low-cost planar modules are designed to fit one on top of the other to create a module stack. The module stack will have a pressure rating, which eliminates the need for a stainless steel pressure vessel and further reduces skid costs. A drawing of a standard shipping container housing several stacks is shown in Figure 3. This containerized skid will be assembled in the fabrication shop with all the required feed, residue, and permeate piping. The completed module skids will be positioned onsite by a crane. Several skids can be stacked on top of one another to minimize capture plant footprint. The containerized skid is the final unit building block for the MTR membrane CO_2 capture process.

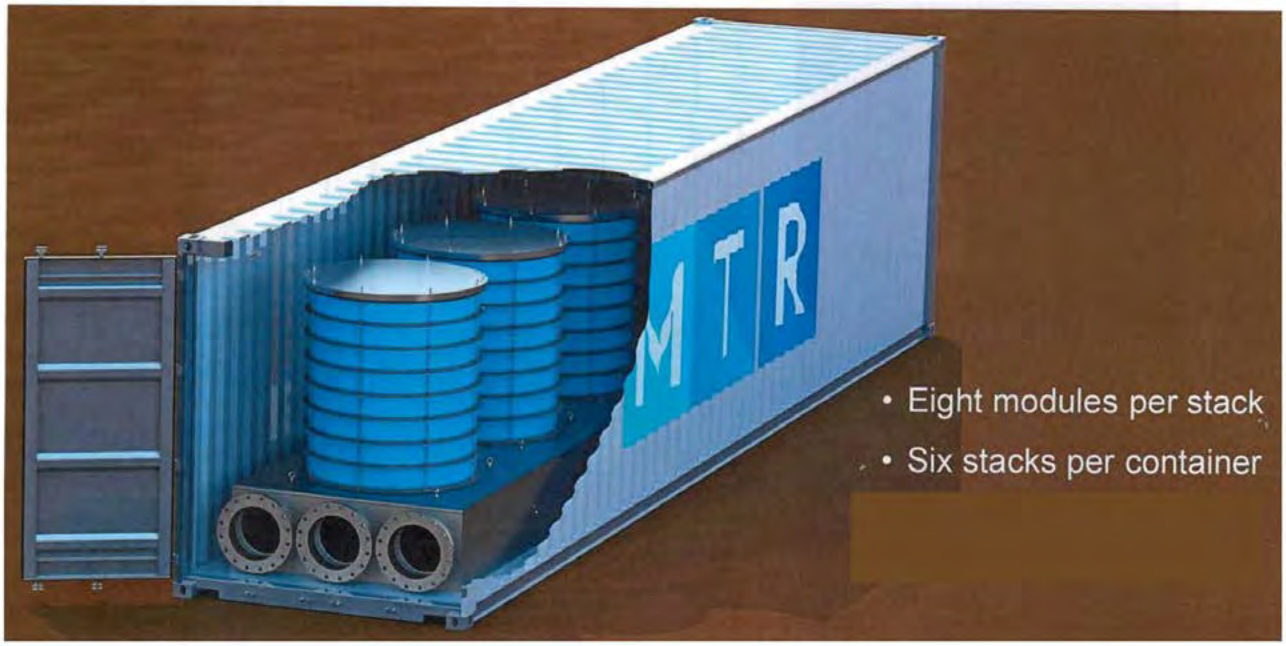

Figure 3: SolidWorks drawing showing the form of a containerized skid housing six membrane module stacks. Each stack is composed of eight modules.

technology advantages

- Capture cost is about 20% lower for cement compared to coal.
- Modular design membrane stacks ideal for scale-up for industrial CO_2 capture.
- High-purity CO_2 (greater than 99.5%) available for offtake at 150 bar.

R&D challenges

Integration and testing of membrane stack at CEMEX testing site.

status

MTR has completed the engineering study and membrane capture of 75% of CO_2 emissions from Kiln 2 at the CEMEX Balcones cement plant. The project is on schedule; the preliminary process design is completed, the capture plant location has been selected, and the design basis is set. The detailed design, costing, and environmental/permitting review has been completed. Reporting of project findings will occur in 2022. The next step is for a pilot demonstration test at Balcones and the completion of the TEA.

available reports/technical papers/presentations

Brice Freeman and Tim Merkel, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11038&filename=Engineering+Design+of+a+Polaris+Membrane+CO2+Capture+System+at+a+Cement+Plant.pdf*.

Alicia Breen, Brice Freeman, Pingjiao Hao, Tim Merkel, Dana Pierik and Kevin Lauzze, Lucia Renau and Nestor Mora, "Engineering Design of a Polaris Membrane CO_2 Capture System at a Cement Plant," 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CCUS_Merkel.pdf*

Cryogenic Carbon Capture from Cement Production

primary project goal

Sustainable Energy Solutions LLC (SES) is partnering with Chart Industries Inc., Eagle Materials Inc., and FLSmidth Inc. to advance a cryogenic carbon capture (CCC) technology to demonstration scale (30 tonnes of carbon dioxide [CO_2] captured/day). The carbon capture unit is being installed at the Eagle Materials/Central Plains Cement Plant in Sugar Creek, Missouri.

technical goals

- Design and size all major process equipment.
- Finalize host site agreements and any required environmental or operational permits.
- Commission and construct the engineering-scale system.
- Operate the constructed system for at least two continuous months within a six-month testing period.
- Demonstrate that the system can achieve at least a 95% carbon capture rate with an exit CO_2 purity of 95% or more.
- Decommission the system and restore the host site to its pre-project state.

technical content

SES has developed a novel carbon capture process using cryogenic technology that exploits the different condensation/freezing points of the components of flue gases in order to separate and capture CO_2. A basic overview of the system is shown in Figure 1. The system works by first cooling the flue gas (state 1). The cooled gas is then sent to a separator (state 2), which removes the solid CO_2 precipitate from the flue gases. Finally, the solidified CO_2 melts under pressure and helps cool the incoming flue gas before being shipped out and stored or utilized (state 3), while the flue gases vent out the stack (state 4). A more detailed view of this system can be seen in Figure 2. The system has been previously demonstrated at skid-scale (1 tonne/day) at power plants, cement plants, heating plants, and several other field locations around the world. The current efforts focus on scaling this system to 30 tonnes/day and operating it over a period of at least two months.

The host site is the Central Plains Cement Plant in Sugar Creek, Missouri, owned and operated by Eagle Materials. This plant operates in two different modes: “raw mill up” (80% of the time) and “raw mill down” (20% of the time). In raw mill up mode, the temperature and CO_2 concentration of the flue gas are lower (90°C versus 220°C and 18% versus 24%), so the CCC system needs to adapt accordingly.

program area:

Point Source Carbon Capture

ending scale:

Small Pilot

application:

Post-Combustion Industrial PSC

key technology:

Novel Concepts

project focus:

Cryogenic-Based CO_2 Capture System for a Cement Production Plant

participant:

Sustainable Energy Solutions LLC (SES)

project number:

FE0032148

predecessor projects:

N/A

NETL project manager:

Carl Laird
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principal investigator:

Larry Baxter
Sustainable Energy Solutions
l.baxter@sesinnovation.com

partners:

Chart Industries; Eagle Materials; FLSmidth

start date:

02.01.2022

percent complete:

2%

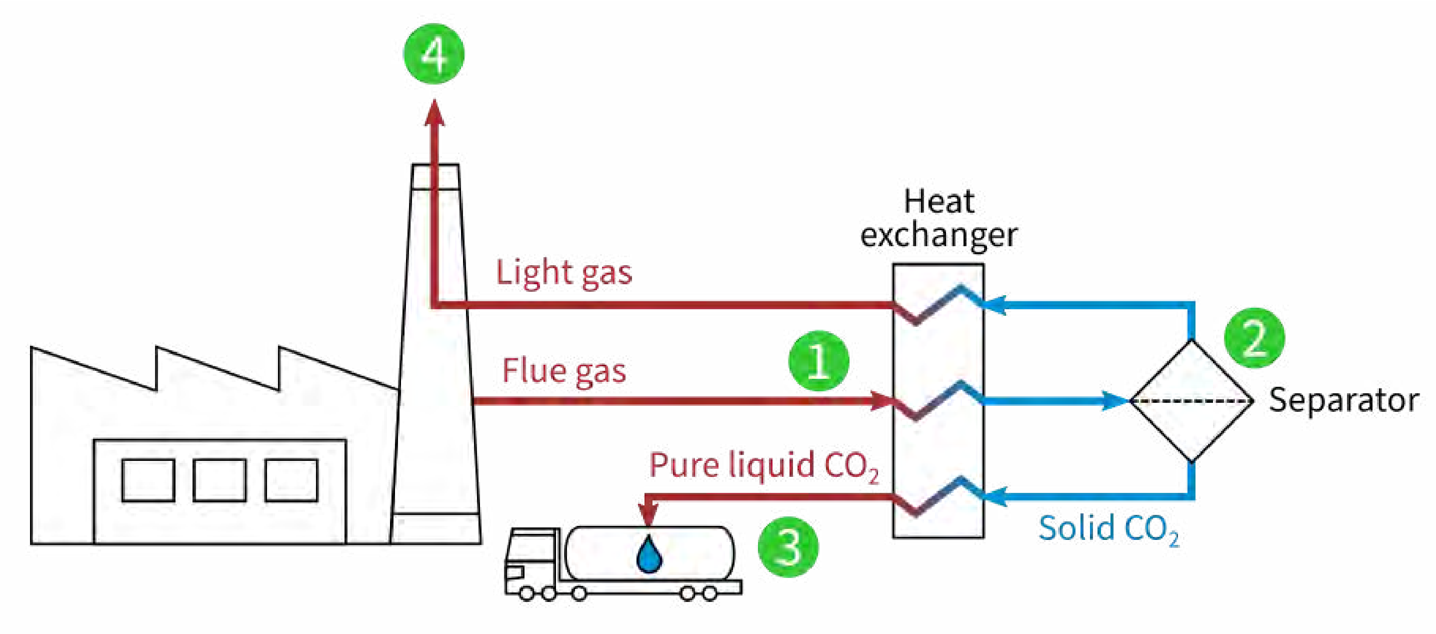

Figure 1: Simplified plant diagram.

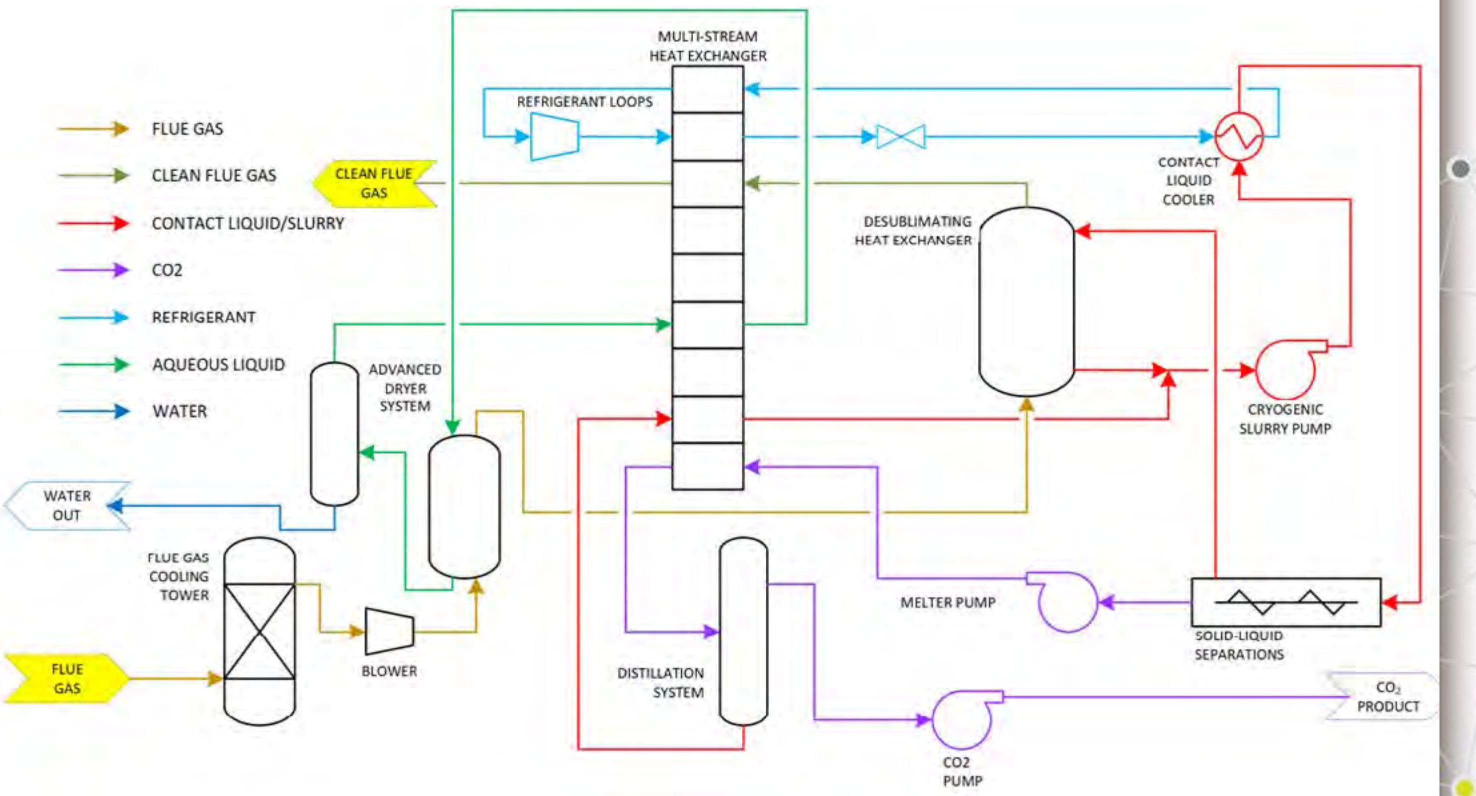

Figure 2: Schematic of CCC system.

Phase I project efforts include a hazard and operability (HAZOP) study and an environmental, health, and safety (EH&S) analysis following completion of the host site agreement. The purpose of these studies is to identify the environmental risks and safety of any future projects that plan to use the proposed capture system. Concurrent with these efforts is the initial design of the plant. Various process and instrumentation diagrams (P&IDs), as well as other detailed construction diagrams, are produced during this task. Finally, all necessary operating and environmental permits are secured in Phase I to ensure the construction phase can proceed.

Final products of Phase I work are: 1) the development of detailed flow simulations to ensure reliable performance and establish initial cost estimates and 2) the sourcing of all major equipment to be used during the construction phase.

Simulations are carried out using commercial Aspen Plus® software. An initial techno-economic analysis (TEA) also is conducted in Phase I.

Project tasks planned for Phase II include finalizing design choices and necessary approvals as well as initiating construction of the final system.

Project tasks planned for Phase III are to analyze the complete system over a six-month period and perform continuous operation for at least two of the six months; decommission the CCC system and restore the plant to its pre-project state; refine simulated models and TEA based on data obtained during testing; compare and reconcile differences in observed and predicted process performance. The current estimated results and target research and development (R&D) values for the costs of capture are shown in Table 1.

TABLE 1: INDUSTRIAL PLANT CARBON CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	27	23
Cost of Carbon Avoided	\$/tonne CO_2	41	35
Capital Expenditures	\$/tonne CO_2	15	13
Operating Expenditures	\$/tonne CO_2	8	6

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Waste Streams Generated – There is no waste stream generation inherent to the CCC process. The water used to cool the inlet flue gas comes in direct contact with the flue gas and may become contaminated with pollutants or particulate matter, which would require water treatment. No other waste streams are expected.

Process Design Concept – The 30 tonnes/day process will be functionally the same and include a similar equipment list as a larger-scale process or system. The process as designed for this site-specific application has a minimum target carbon capture rate of 95%, and a CO_2 purity target of 99.97%.

Proposed Module Design – SES is using a skid-based system design for this project, which allows much of the equipment to be built offsite and minimizes construction onsite. This system is shown in Figure 1. Chart Industries is supporting this skid-based design with both engineering support and in the construction of various coldboxes used in the system.

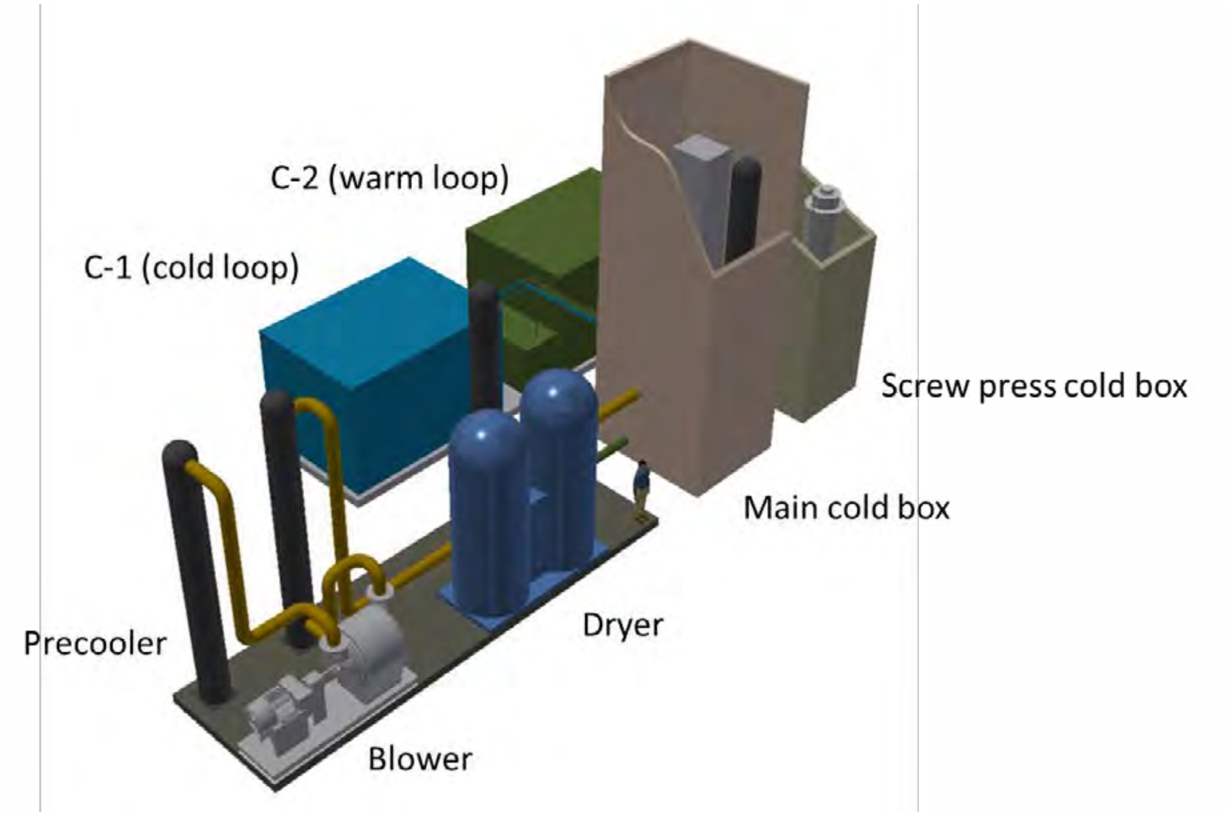

Figure 1: Preliminary design for skid-based CCC system.

technology advantages

- High carbon capture rate (95–99.7%).
- Easy to retrofit onto existing plants.
- Integrated grid-scale energy storage.
- Lower cost than traditional amine sorbents.
- Lower water usage than traditional amine sorbents.
- Robust operation with pollutants such as nitrogen oxide (NO_X) and sulfur oxide (SO_X) and partial co-capture of these pollutants.

R&D challenges

- Keeping energy usage low.
- Achieving continuous capture efficiency, even as cement plant changes operational modes.
- Scaling novel process equipment to small-industrial scale.

status

Project has commenced and a kickoff meeting was held on April 1, 2022.

available reports/technical papers/presentations

Stitt, K., 2022, “Cryogenic Carbon Capture from Cement Production.” Project Kickoff Meeting. National Energy Technology Laboratory: Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=13130&filename=Cryogenic+Carbon+Capture+from+Cement+Production.pdf*.

Blue Bison ATR Advanced CCUS System

primary project goal

Tallgrass MLP Operations LLC is partnering with the University of Wyoming and Technip Energies to perform an initial engineering design of a commercial-scale carbon capture and storage (CCS) system installed at a hydrogen (H_2) production plant proposed to be installed in Douglas, Wyoming. The proposed plant would produce decarbonized H_2 from natural gas (or "blue" H_2), utilizing Haldor Topsøe's auto-thermal reforming (ATR) technology coupled with BASF's OASE® White carbon capture system. The primary project goal is to complete an initial design of a commercial-scale advanced carbon capture, utilization, and storage (CCUS) system that separates, stores, and utilizes more than 100,000 tonnes per year net CO_2 with 90%+ carbon capture efficiency—from an ATR facility producing high-purity H_2 from natural gas—providing a basis for subsequent deployment of CCUS projects of this type.

technical goals

- Design a commercial-scale carbon capture system that could be installed and fully integrated with a 220-million standard cubic feet per day (MMSCFD) blue H_2 facility utilizing ATR technology, producing 99.97% pure H_2 delivery pressure at or above 360 pounds per square inch absolute (psia).
- Establish system capability of meeting CO_2 capture requirements of 95% pure CO_2 with 90+% capture efficiency, CO_2 delivery pressure at or above 2,215 psia, and a goal for CO_2 transport and storage costs at or below $10 per tonne.
- Identify potential utilization pathways for CO_2 and H_2.
- Determine levelized cost of hydrogen and cost of carbon capture to help achieve the U.S. Department of Energy's (DOE) target for carbon-neutral blue H_2 production of less than $1 per kg.

technical content

The proposed site for the H_2 production plant with integrated capture is adjacent to Tallgrass' midstream gas processing plant in Douglas, Wyoming (see Figure 1). This location has multiple favorable characteristics:

- Immediate proximity to existing natural gas lines and existing gas processing plant with its infrastructure and utilities.
- Plausible regional market options for blue H_2 utilization in power generation, renewable diesel production, decarbonized ammonia production in the Midwest, and transportation uses.
- Options for CO_2 utilization with storage opportunities within 1 mile of the host site, enhanced oil recovery (EOR) fields in the regions, and the Wyoming CO_2 corridor initiative.

program area:

Point Source Carbon Capture

ending scale:

pre-FEED

application:

Pre-Combustion Industrial PSC

key technology:

Solvents

project focus:

BASF's OASE® White Carbon Capture System with Natural Gas Reforming

participant:

Tallgrass MLP Operations LLC

project number:

FE0032114

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Jeff Schaefer
Tallgrass MLP Operations LLC
jeff.schaefer@tallgrassenergylp.com

partners:

University of Wyoming;
Technip Energies

start date:

10.01.2021

percent complete:

5%

Figure 1: Proposed project site.

The proposed H_2 production plant would leverage Haldor Topsøe's SynCOR™ ATR technology (see Figure 2). SMR is the most common natural gas reforming technology deployed, but SMR produces CO_2-loaded flue gas requiring post-combustion capture. However, in ATR, most of the CO_2 generated can be efficiently captured from the high-pressure raw synthesis gas (syngas) stream via amine scrubbing. Unlike SMR, ATR requires oxygen input, but for high CO_2 capture rates the ATR approach is preferred to SMR. The SynCOR ATR technology is oxygen-blown, featuring an adiabatic reformer upstream to convert heavy feedstocks to methane and a fired heater to preheat the feed natural gas, and a high-pressure steam byproduct is used to generate power in a steam turbine generator, which can offset the power demand of the air separation unit (ASU) needed for oxygen production.

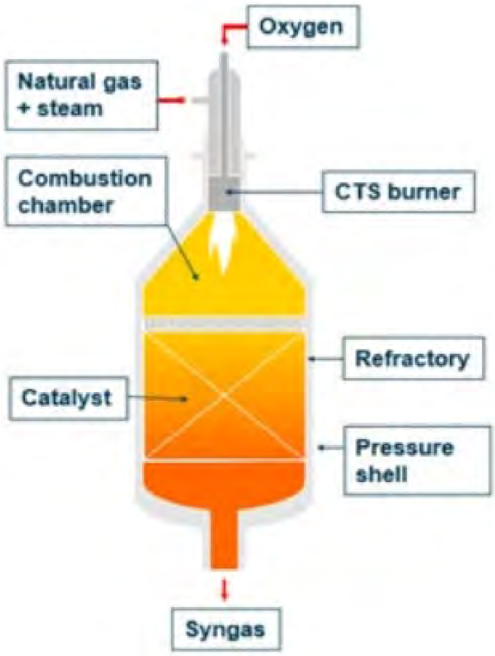

Figure 2: SynCOR™ autothermal reformer.

The integrated H_2 production plant would integrate the autothermal reformer with deep water-gas shift (WGS) and thorough CO_2 capture via BASF's OASE white carbon capture system. The overall process concept for the integrated plant is depicted in Figure 3.

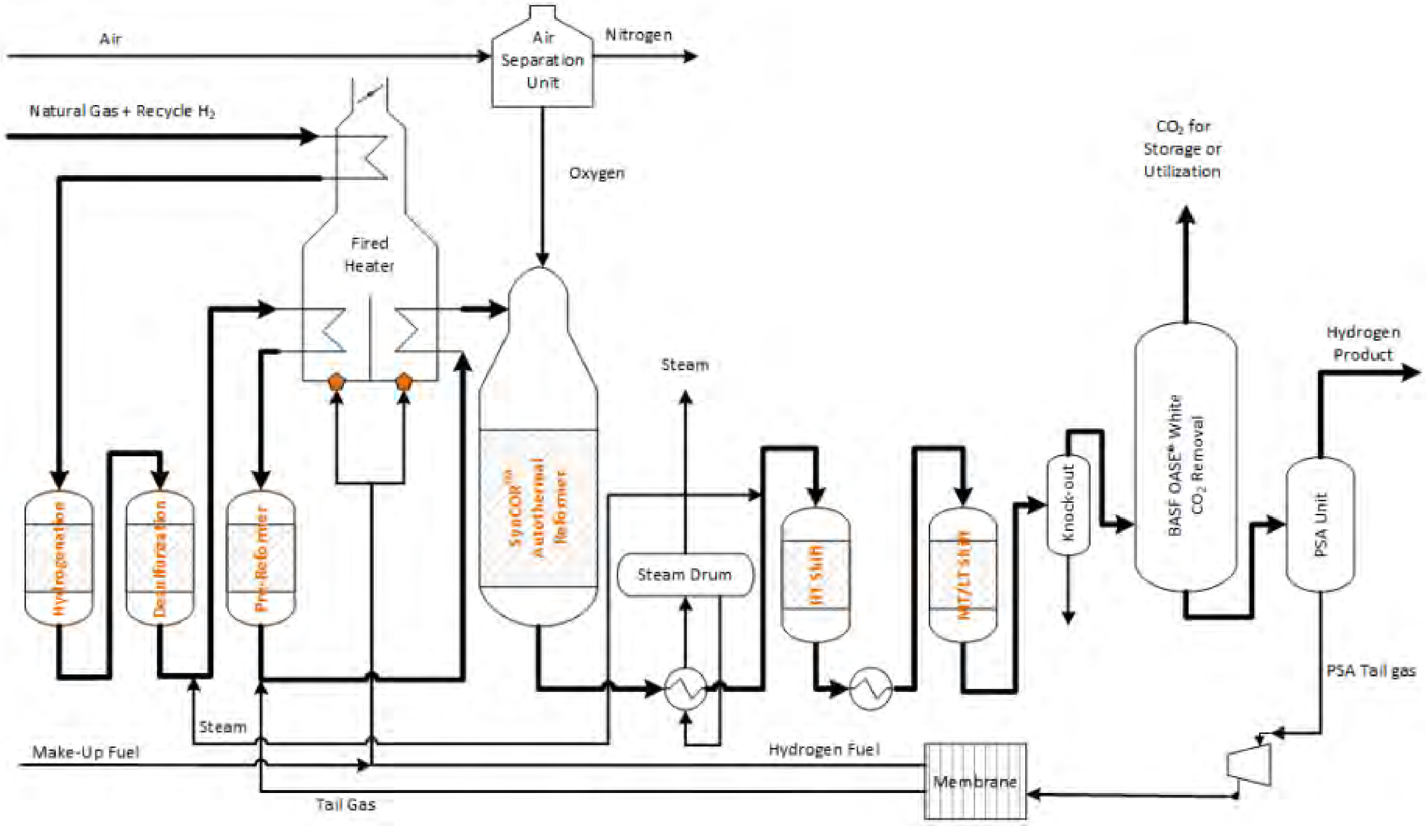

Figure 3: Process concept for integrated ATR with CO_2 capture.

BASF's OASE white is a state-of-the-art amine solvent-based technology for pre-combustion capture of CO_2 from syngas. It is a high-efficiency process, requiring low energy consumption per ton CO_2 captured.

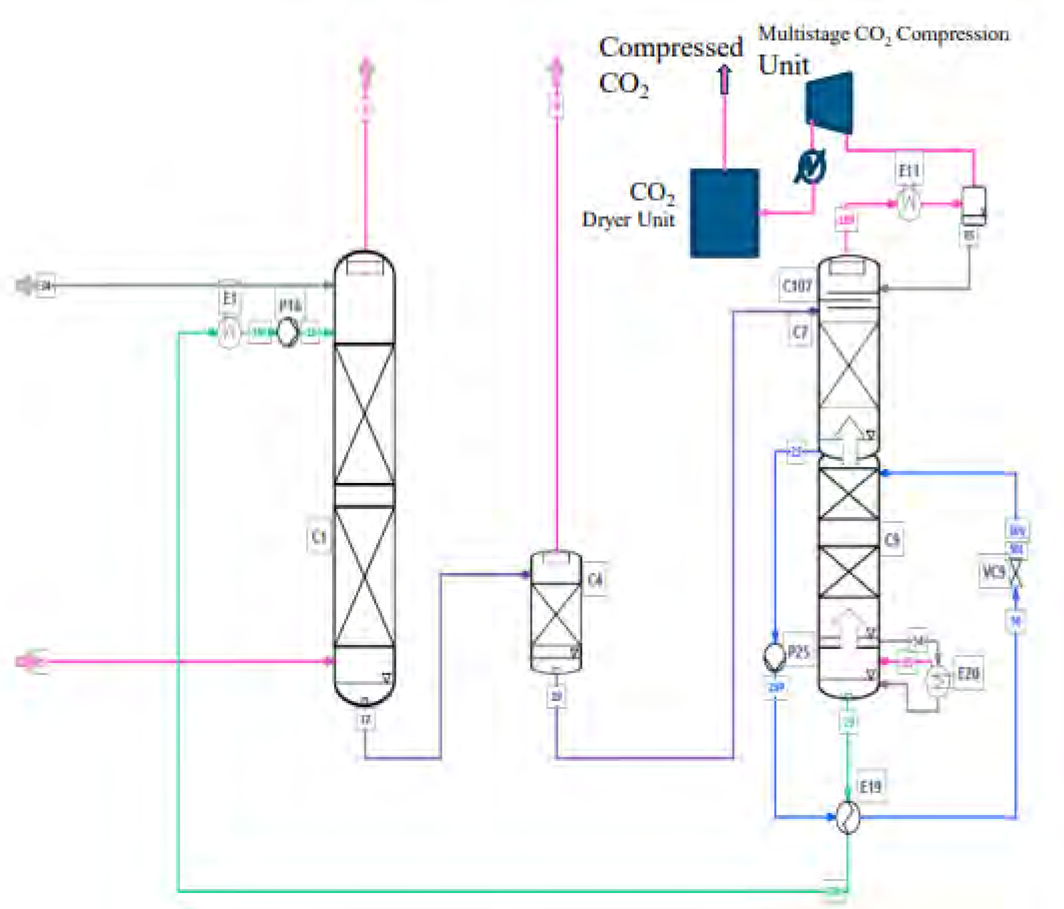

Figure 4: BASF OASE® White carbon capture technology.

*TABLE 1: SOLVENT PROCESS PARAMETERS

Proposed Module Design			(for equipment developers)	
Syngas Flowrate	kg/hr		219,160	
CO_2 Recovery, Purity, and Pressure	% / % / bar	99.9	99.57	152
Absorber Pressure Drop	bar		0.2	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		—	

*Numbers presented in this document represent best current information

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Combination of physical and chemical.

Solvent Contaminant Resistance – Currently unknown.

Solvent Foaming Tendency – Currently unknown.

Flue Gas Pretreatment Requirements – Currently unknown.

Solvent Makeup Requirements – Currently unknown.

Waste Streams Generated – Currently unknown.

Process Design Concept – See Figure 3.

Proposed Module Design – See Figure 4. The pressure, temperature and composition of the gas entering the module are as follows:

Pressure	Temperature	Composition entering BASF module						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	Ar+N_2	H_2	H_2O	H_2S
378	60	24.7	0.58	0.82	0.49	72.65	0.77	0

Technology advantages

- State-of-the-art, commercially proven technologies for syngas generation and treatment.

R&D challenges

- Developing a mechanical design for the largest advanced heat exchanger reformer (TPR®), which can be integrated with the ATR to reduce O_2 consumption and minimize methane (CH_4) slip from the TPR.
- Verifying test data for use of pure blue H_2 as fuel in LSV® burners in the ATR preheater to minimize or eliminate CO_2 production in the fired heater.

status

The project team has developed utility flow digrams, piping and instrumentation diagrams, and heat and material balances. A 3D model of the system is being generated.

available reports/technical papers/presentations

"Blue Bison DE-FE0032114 Kickoff Meeting," Kickoff Meeting Presentation, October 19, 2021.
https://netl.doe.gov/projects/plp-download.aspx?id=11230&filename=Blue+Bison+DE-FE0032114+Kickoff+Meeting.pdf

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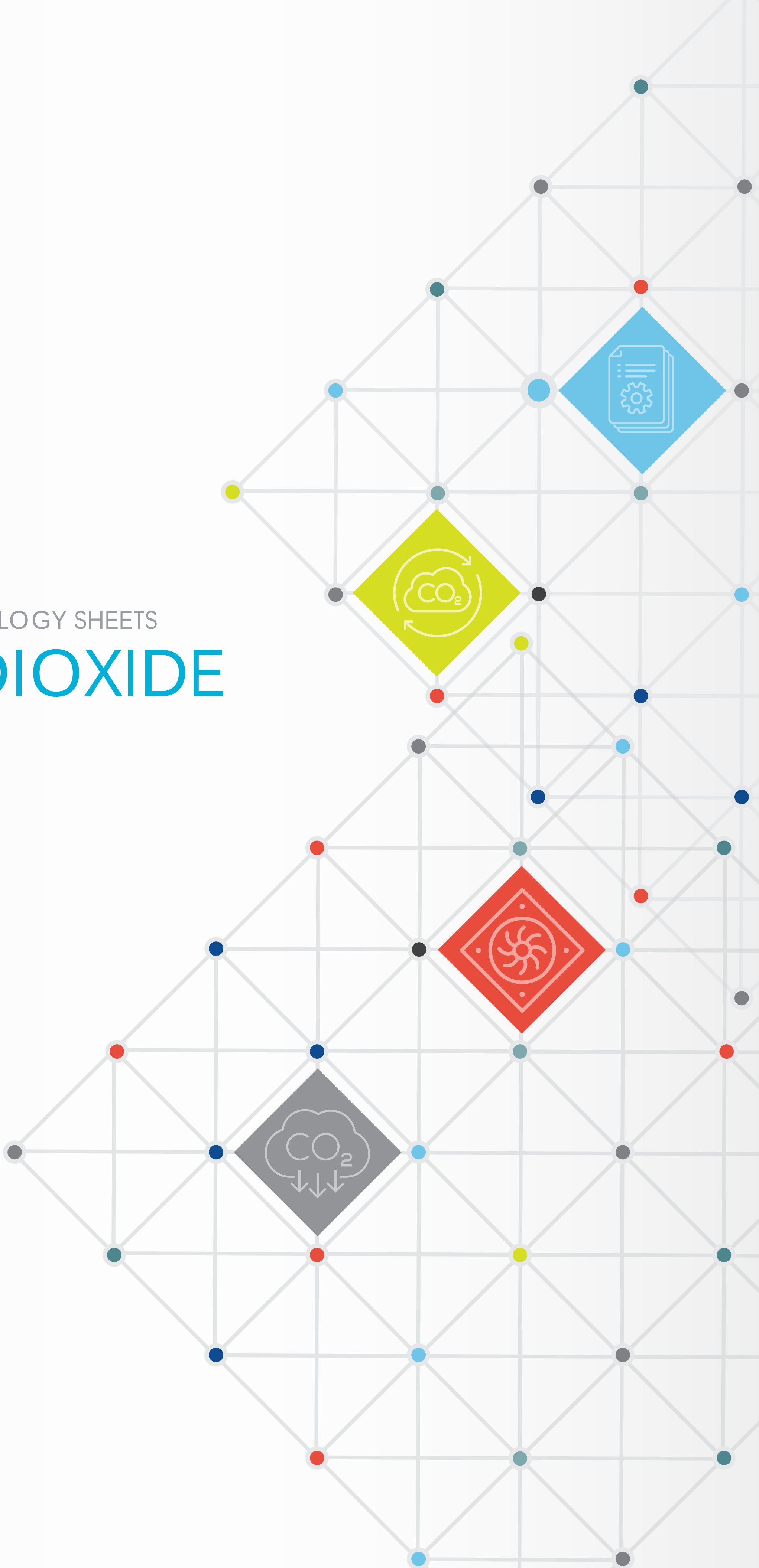
CARBON CAPTURE TECHNOLOGY SHEETS

CARBON DIOXIDE REMOVAL



Spatiotemporal Adaptive Passive Direct Air Capture

primary project goal

Carbon Collect Inc., along with the Electric Power Research Institute (EPRI), Arizona State University (ASU), Trimeric Corporation, and PM Group, is performing an initial design of a commercial-scale, passive direct air capture (DAC) system termed “Carbon Trees” to capture, separate, and store or utilize a nominal capacity of 1,000 tonnes per day of carbon dioxide (CO_2) from air.

technical goals

- Prepare an initial engineering design package for carbon farms based on the Carbon Tree technology at each of three geographically diverse host sites throughout the United States to better understand the effect of local/regional ambient conditions on DAC system performance and project costs.
- Complete a techno-economic analysis (TEA), life cycle analysis (LCA), business case analysis, and an environmental, health, and safety risk assessment for each of the three geographically diverse host sites.

technical content

Passive DAC is unique among DAC technologies in that passive air delivery by wind avoids the energy penalty of forced convection. The passive DAC Carbon Tree system includes a passive collector that absorbs wind-delivered CO_2 and an integrated regenerator that releases CO_2 into a confined chamber. During CO_2 collection, the leaves of the Carbon Tree take the form of large horizontal disks arranged in a vertical column over a cylindrical regeneration chamber. For sorbent regeneration, the column lowers into the chamber; a combination of steam, low-grade heat, and vacuum releases the CO_2, which is extracted from the chamber and then purified and compressed.

Uniquely, this system readily accommodates alternative hybrid cycles—temperature vacuum swing absorption (TVSA), moisture vacuum swing absorption (MVSA), moisture temperature vacuum swing absorption (MTVSA), and their associated alternate sorbents—such that the collector system is adaptable to broadly different climate conditions. This study will illustrate and emphasize this unique advantage, employing both TVSA and MTVSA cycles as appropriate for the three study sites. For both of these cycles, the collector effluent gas is a mixture of CO_2 and water (H_2O) with trace residual air. The collector effluent is compressed and purified to storage-ready specifications by a compression and purification unit (CPU). The CPU comprises conventional unit operations that are configured to recapture nearly 100% of heat and water for a nearly closed cycle integration with the collector and optimal energy efficiency. The Carbon Tree design represents a radical departure from other forced-air DAC systems. Instead of using fans and blowers to force air, the contactor in its fully open position (Figure 1, right) stands in the native wind to capture CO_2 directly from passing ambient air onto leaf-like structures containing sorbent. The system’s vertical column incorporates a stack of 150 1.5-decimeter (dm) disks that hang freely on straps, forming a 7.5-meter column above the regenerator chamber. Wind flows freely through gaps between these disks while about 30% of the CO_2 is fractionally skimmed from the air stream.

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Dynamic Performance of Passive “Carbon Tree” DAC Technology

participant:
Carbon Collect Inc.

project number:
FE0032097

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
Arizona State University; Electric Power Research; Institute; PM Group; Trimeric Corporation

start date:
10.01.2021

percent complete:
12%

Figure 1: Carbon Tree in capture (right) and regeneration modes (left).

The disk frames shown in Figure 2 provide support structure to hold a variety of sorbent materials and form factors with high surface area exposure. For regeneration, the column is lowered into the regeneration chamber, collapsing the disk stack. The chamber is pre-evacuated to rough vacuum to remove bulk air contamination and heated with sub-atmospheric steam to between 40–100°C, releasing CO_2 at a vapor pressure of about 5 kPa. The MTVSA cycle uses steam principally as a sweep gas to carry liquid water droplets as an aerosol to the MTVSA sorbent. In both TVSA and MTVSA cycles, the steam increases the total pressure during regeneration to significantly reduce the vacuum requirement. Steam is the condensed from the regeneration effluent for energy recovery and bulk water removal. The remaining gas comprising CO_2 with residual water and air is subsequently compressed and purified in the CPU as described below.

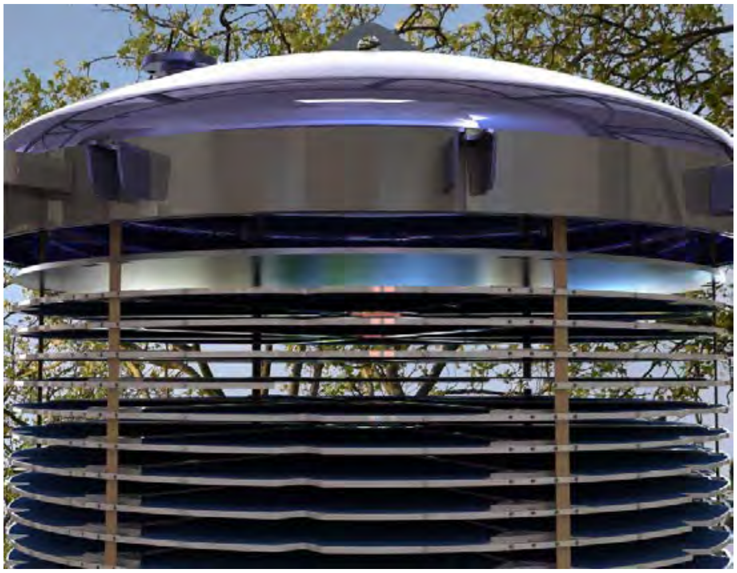

Figure 2: Top head and disks of Carbon Tree.

Starting with a durable sorbent that has been demonstrated in outdoor operation for more than a year, the temperature tolerance of the sorbent was increased so as to take better advantage of the heat of condensation of the water used to deliver these sorbents. The current sorbent receives a substantial boost from the increase in moisture, but by raising the temperature, this project can reach even higher concentrations and forgo the moisture boost in humid climates. ASU and, more recently Carbon Collect Limited (CCL), have worked over the past 10 years to build a library of sorbents and form factors to allow the fine-tuning of the Carbon Tree system for geographically diverse host sites. Without major hardware changes, sorbent selection, and the application of heat, vacuum and moisture can be optimized (patents pending). Detailed thermodynamic analyses of the role of water and heat in these sorbents have been developed. An MVTSA commercial system will require less than 70 kJe/mol or 440 kWh per tonne of final product CO_2.

technology advantages

- Passive DAC uses wind delivery of air which lowers operating expenses (OPEX).
- Reduction in capital expenditure (CAPEX) using economies of mass production of inexpensive modular equipment.

R&D challenges

- Optimizing collector to minimize temperature, thermal mass, and void space.
- Cycle optimization for efficient water and thermal energy recovery.

status

Trimeric is currently beginning the process design basis and initial development of the engineering design of the process. This includes the establishment of site-specific data, design specifications, ambient conditions, potential permitting requirements, process targets for CO_2 capture, and purity. The PM Group is beginning site planning, layout, and tree design. EPRI is beginning the geological storage assessment of the three site locations (Southern San Joaquin Valley; Citronelle, Alabama; and Gillette, Wyoming), estimating capital operating costs of injecting and storing CO_2 for project scenarios, etc.

available reports/technical papers/presentations

Mike Austell, "Spatiotemporal Adaptive Passive Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, November 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12348&filename=Spatiotemporal+Adaptive+Passive+Direct+Air+Capture.pdf*.

Direct Air Capture-Based Carbon Dioxide Removal with U.S. Low-Carbon Energy and Sinks

primary project goal

The University of Illinois is leading a team to develop preliminary designs for large-scale direct air capture (DAC) plants that separate and permanently store 100,000 tonnes/yr net carbon dioxide (CO_2) from the air at three different facilities located in Wyoming, Louisiana, and California. The project goal is to examine the effect of various climatic conditions on the DAC system design and overall cost and evaluate the impact of using different low-carbon energy sources (i.e., geothermal, solar, wind, or waste heat). Further, this work aims to tackle scale-up challenges related to construction, operation, and logistics, as well as gauge the technical and regulatory challenges at each site.

technical goals

- Perform an initial engineering design, techno-economic analysis (TEA), life cycle analysis (LCA), business case analysis, and an environmental health and safety (EH&S) analysis for a commercial-scale carbon capture and storage (CCS)-DAC system to capture 100,000 tonnes/year net CO_2 from the air. Produce the designs for the three proposed host site locations.
- Prepare a capital cost estimate (Class IV) for a CCS-DAC system for each of the host sites. Use the capital costs to estimate \$/tonne CO_2 net captured.

technical content

Globally, eight countries and states have legally binding net-zero targets, supported by 127 countries and states with net-zero goals (not yet legally binding). Private industry is also reacting, with more than 1,300 companies having net-zero targets (as of January 2022). Globally, net-zero commitments cover at least 68% of the global economy (USD \$84.6 trillion). Meanwhile, recent scientific analyses support a widespread, massive investment in DAC deployment as a solution to the climate crisis. Climeworks is the world's first company to demonstrate DAC in combination with geological CO_2 storage (Figure 1) and has successfully created a business model based on the sales of carbon dioxide removal (CDR) services. Climeworks has remained the global market leader in this area, continuing to operate the world's only pre-commercial-scale DAC systems today, and continuing to add to its CO_2 capture capacity. Strategically, Climeworks prioritizes climate-positive CDR.

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Scale-up of Climeworks' Sorbent-Based DAC Technology

participant:
University of Illinois

project number:
FE0032100

predecessor projects:
N/A

NETL project manager:
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partners:
Climeworks; Kiewit; LLNL; Ormat; GCS; SunPower; NSE

start date:
10.01.2021

percent complete:
17%

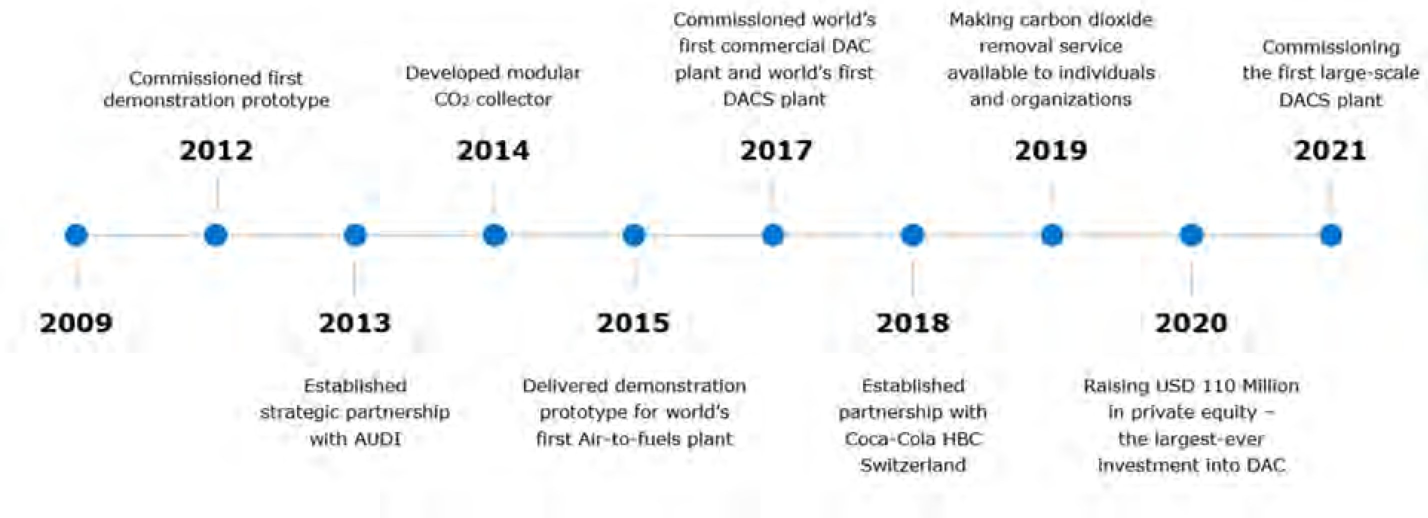

Figure 1: Climeworks' company history. (DACS = direct air capture with storage.)

Climeworks' DAC plants capture atmospheric CO_2 by applying a cyclic vacuum-temperature swing adsorption and desorption process, described below and schematically illustrated in Figure 2.

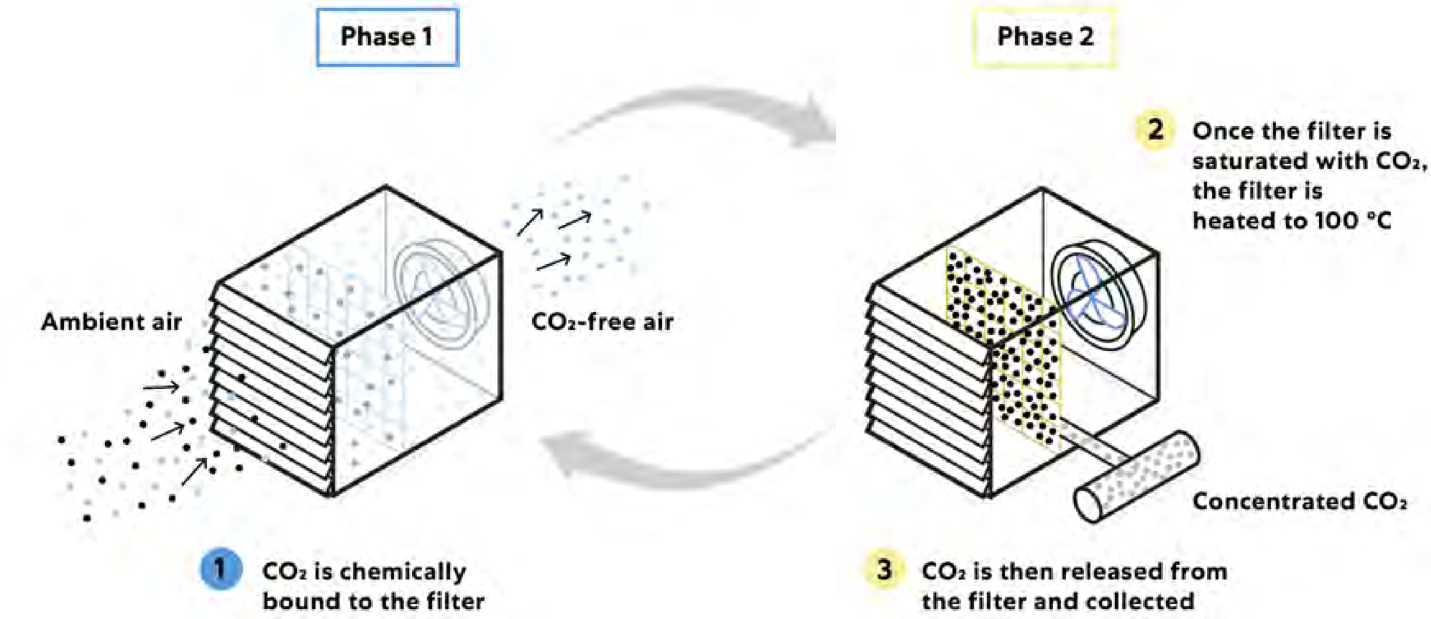

Figure 2: Working principle of Climeworks' DAC technology. Phase I produces CO_2-depleted air and binds the CO_2 on the filter. Phase II produces pure CO_2 and regenerates the sorbent.

Phase I (Adsorption): Air is drawn into the plant using fans and the CO_2 within the air is chemically bound to the sorbent, a highly selective filter material, henceforth also referred to as "filter." Carbon-dioxide-depleted air is released back into the atmosphere.

Phase II (Desorption): Once the filter is saturated with CO_2, it is heated under vacuum to around 100°C using low-grade heat as an energy source. The CO_2 is then released from the filter and collected as a concentrated gas and the continuous cycle is ready to start again. The filter material lasts for several thousand cycles (i.e., several years).

This technology is based on a decade of research and development (R&D) activities, largely in collaboration with world-leading research institutes at the Swiss Federal Institute of Technology (ETH Zurich) and the Swiss Federal Laboratories for Materials Science and Technology. The filter material is arranged in a patented adsorber structure (called "contactor") optimized for low pressure drop and high air flow rates in order to maximize CO_2 capture at the lowest fan electricity cost.

These contactors are contained inside so-called "CO_2 collectors," where the filter is exposed to ambient air in Phase I and where the CO_2 is subsequently extracted from the filter in Phase II, as shown schematically in Figure 2 above.

Climeworks' proven technology has captured CO_2 from air at a pre-commercial scale for more than three years, at 24/7 operation, for a capacity of about 900 tonnes CO_2/year at Climeworks' Beta plant in Hinwil, Switzerland (Figure 3). Scale-up and further cost reductions are now the largest challenges for this technology to meet the increasing global demand for negative emissions. Currently, Climeworks is building the world's largest DAC facility (Orca plant, 4,000 tonnes CO_2/year, for storage) in Iceland, commissioned in September 2021.

	DAC only	DAC and geological storage for permanent CDR		
	Pre-commercial DAC plant ("Beta")	First CDR Pilot ("Arctic Fox")	First-of-a-kind demonstration ("Orca")	Commercial demonstration
Start of operation	2017	2017	2021	2025
CO_2 Collector design				
Arrangement of CO_2 Collectors	6 Collectors per container	1 Collector standalone	6 Collectors per container	1 Collector per container
Sealing of CO_2 Collectors	2 flaps per Collector	2 flaps per Collector	1 sliding door per container	1 sliding door per Table of containers
DAC Plant design				
Nominal CO_2 capacity of plant/per container [t/yr.]	900/300	50/50	4,000/500	100,000/750

Figure 3: Climeworks' development history positions its technology for large-scale implementation today.

Climeworks is advancing its scale-up roadmap to demonstrate large-scale commercial-size DAC at up to 100,000 tonnes CO_2/year with this project. In the current generation, the current cyclic adsorption/desorption technology generation is now mature; it has been optimized across collector geometry, adsorption settings, and desorption settings to result in a maximized output per DAC collector unit using current sorbent technology. The DAC collectors' modular nature and the flexibility of the integrated contactor structures ensure that future developments in sorbent technology can be easily integrated into existing hardware.

The case studies for this project represent different climatic conditions as well as a variety of environments for CO_2 storage from saline aquifers to depleted natural gas reservoirs for safe and permanent storage. Furthermore, the energy supply of the DAC plant differs in each case study and represents a broad variety of low-carbon energy solutions.

Definitions:

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_X**	**NO_X**
ambient	ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Amine-based sorbent which binds CO_2 by chemisorption, as described in Phases I/II of Figure 2.

Sorbent Contaminant Resistance – Sorbent is highly resistant to expected contaminants found in the air. Sulfur oxide (SO_X) and nitrogen oxide (NO_X) at levels present in most air streams are not a key driver of degradation.

Sorbent Attrition and Thermal/Hydrothermal Stability – Stability of sorbent over thousands of cycles has been demonstrated by Climeworks' operating DAC plants.

Air Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Replacement of sorbent required every three years (equivalent to several thousand cycles).

Waste Streams Generated – Carbon-dioxide-depleted air is emitted from the contactors. Water is treated and reused in the plant (at full-scale).

Process Design Concept – A block flow diagram detailing the two phases of the project is shown in Figure 3.

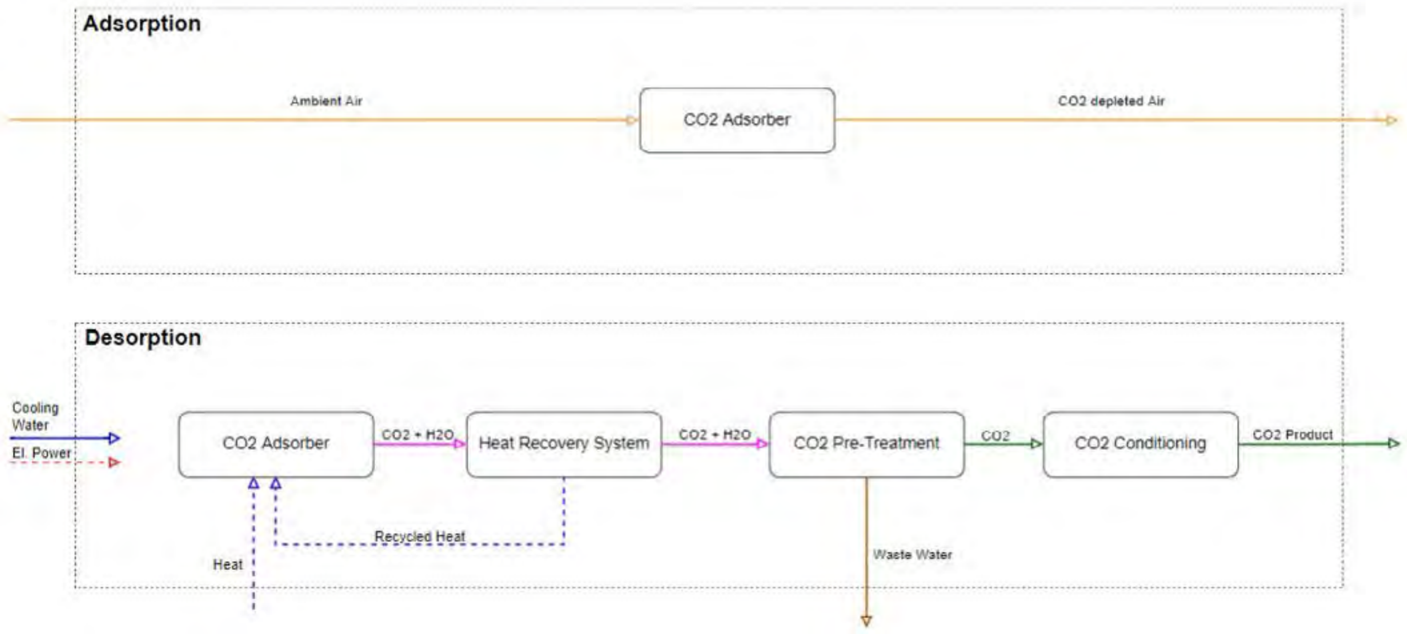

Figure 3: Block flow diagram.

Proposed Module Design – The sorbent is located inside a CO_2 Collector Container (CC). The concept of modular CCs was first developed in 2014 for the first generation of Climeworks plants. Its modularity allows for easy scale-up (the number of collectors can be adapted to match the required capacity per plant) and production can benefit from economies of scale. This CC has the external dimension of an ISO 668 40-ft container, to allow for simpler handling and shipping.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Estimate 2035**	Target long-term
Cost of Carbon Removed	\$/tonne CO_2	150-210	~100
Cost of Net Negative Emissions achieved*	\$/tonne CO_2	170-230	~110
Capital Expenditures	% of total	30-50%	
Operating Expenditures	% of total	50-70%	

*** Including a full life cycle assessment from cradle-to-grave.**
**** At 1 $MtCO_2$/y single plant scale, with a learning rate consistent with total installed volume of 100 $MtCO_2$/y assumed.**

Definitions:

Cost of Carbon Removed – Projected cost of capture and storage per mass of CO_2 under expected operating conditions.

Cost of Net Negative Emissions Achieved – Projected cost of capture and storage per mass of CO_2 when accounting for the associated grey emissions.

Capital Expenditures – Projected capital expenditures in percentage of total costs.

Operating Expenditures – Projected operating expenditures in percentage of total costs.

Calculations Basis – Calculations above consider a 1 $MtCO_2$/year single plant, using capital cost values derived from Climeworks' current plants, with scaling factors in the range of 0.6–0.95 depending on the equipment type, with forecasted renewable electricity and heat prices, and with a learning rate assumed for future generations of plants equivalent to a total installed volume of 100 $MtCO_2$/y.

Scale of Validation of Technology Used in TEA – The Climeworks DAC systems consist of three major subsystems: the core technology (optimized sorbent/process combination); the full-scale modular CO_2 collectors, which house the core technology; and the process plant. This project focuses on the improvement of the process plant and optimization of a large-scale plant (layout and equipment optimization).

"Estimate 2035" costs are based on development improvements of the core technology, as well as incremental improvements of Climeworks' current systems for the collectors and process plant, based on field-proven enhancements of the Orca plant in Iceland.

Qualifying Information or Assumptions – A conservative 90% removal efficiency (net-negative emissions CO_2 achieved/CO_2 removed) is assumed, consistent with external LCAs performed of Climeworks' systems.

technology advantages

- Mature plant design, from the extensive experience in designing, constructing, and operating full-system prototypes, as well as up to 4,000 tonnes CO_2/year pre-commercial units.
- Modular design of the CCS-DAC plants enables Climeworks to scale rapidly from a pre-commercial to commercial scale.
- DAC collector modular nature allows flexibility for future developments in sorbent technology, which can be easily integrated into existing hardware.

R&D challenges

- Engineering design of DAC systems at three different host sites with differing climates.

status

The University of Illinois has begun initial engineering design and initial planning, collecting information and requirements for each host site.

available reports/technical papers/presentations

Kevin C. Obrien, "Direct Air Capture-Based Carbon Dioxide Removal with United States Low-Carbon Energy and Sinks," Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11215&filename=Direct+Air+Capture-Based+Carbon+Dioxide+Removal+with+United+States+Low-Carbon+Energy+and+Sinks.pptx*.

Kevin C. Obrien, "Direct Air Capture Facility Development in the United States," presented at American University's Assessing Carbon Removal webinar series, February 21, 2022. *https://www.youtube.com/watch?v=HX5c3llo42w*.

Scale-Up and Site-Specific Engineering Design for Global Thermostat Direct Air Capture Technology

primary project goal

Black & Veatch Corporation is partnering with Global Thermostat (GT), Sargent & Lundy, ExxonMobil Research and Engineering, Southern Company Services, and Elysian Ventures LLC to execute an initial engineering design of a commercial-scale carbon capture, utilization, and storage direct air capture (CCUS-DAC) system that captures at least 100,000 net tonnes/year of carbon dioxide (CO_2) from the atmosphere. The lead system, designated as DAC+, consists of a DAC unit utilizing GT's sorbent contactor technology coupled with a natural gas-fired combined heat and power (CHP) plant, the DAC+ designation indicating modification of the DAC system to enable capture of the CHP unit flue gas.

technical goals

- Complete the baseline design of the commercial-scale DAC+ unit that captures CO_2 from both the air and the associated natural gas-fed CHP unit, for a *net* removal of 100,000 tonnes of CO_2 per year from the atmosphere.
- Conduct site-specific studies for three proposed plant site locations: Odessa, Texas; Bucks, Alabama; and Goose Creek, Illinois.
- Conduct a comparative study of DAC+ versus DAC combined with a traditional post-combustion carbon capture system for at least one of the potential host sites.
- Develop a techno-economic analysis (TEA), life cycle analysis (LCA), and environmental health and safety (EH&S) analysis to compare the cost, emissions, and performance metrics between all three proposed site locations.

technical content

The project utilizes a polymer-based adsorbent system developed by GT in 2009. The process container for the GT system, displayed in Figure 1, uses a temperature-vacuum swing adsorption (TVSA) regeneration cycle to remove CO_2 from both the air and flue gas. Steam is used as a direct phase-change heat transfer fluid to remove the CO_2 from the adsorbent. The proprietary adsorbent material uses a honeycomb geometry, which has been experimentally verified to have a very low pressure drop, which helps minimize energy cost. The system is designed to be modular: each module is about 250 cubic feet in size (2,000 cubes that are 6 by 6 by 6 inches), and scale-up can be achieved by adding more modules in an array.

The complete absorption-regeneration cycle is designed to operate in DAC+ mode, where air and flue gas are passed through the adsorbent filter honeycomb sections sequentially to maximize carbon capture capacity. The overall process targets about 1,000 seconds to complete cycle for a single module, as indicated in Figure 2. The illustrated unit contains 10 sorbent panels, which move in a counter-clockwise manner to enable stationary positioning in the regeneration box (shown as gray area in the figure).

program area:
Carbon Dioxide Removal

ending scale:
pre-FEED

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Sorbent-Based DAC+ System Integrated with Combined Heat and Power (CHP) Plant

participant:
Black & Veatch

project number:
FE0032101

predecessor projects:
N/A

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partners:
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start date:
10/01/2021

percent complete:
10%

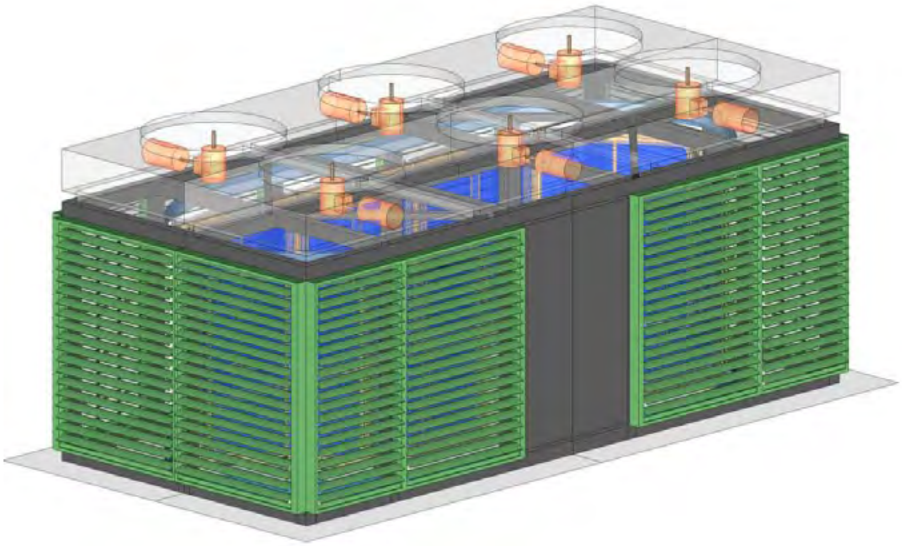

Figure 1: 3D rendering of GT's DAC system, with nine stations for sorption and one station for harvest/regeneration (gray area in Figure).

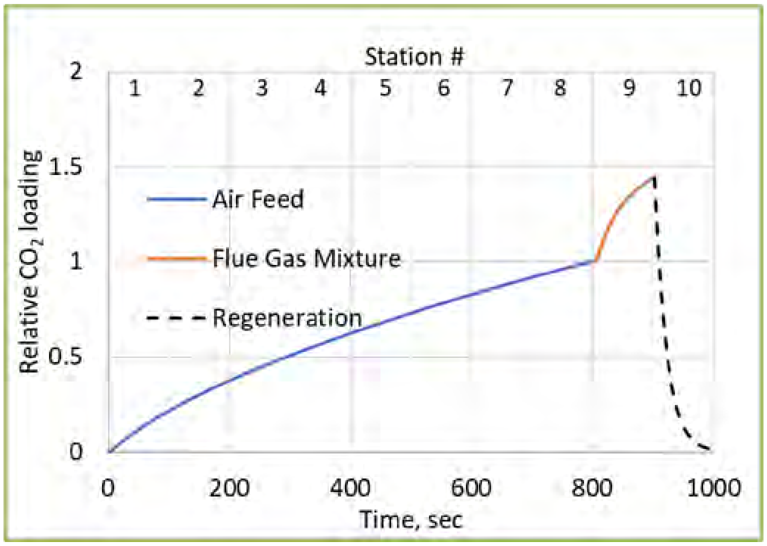

Figure 2: Laboratory adsorption data as a demonstration of the operation of a DAC+ unit. Air feed is 400 ppm; flue gas mixture is 10,000 ppm.

The proprietary adsorbent material's known properties and the operating parameters of the adsorption-regeneration system are shown in Table 1. The TVSA system works by manipulating the temperature and pressure of the adsorbent material in order to change the adsorptivity of the material to prioritize either adsorption or desorption at the right time, selectively removing CO_2 from the feed gas or releasing the CO_2 in order to transport it to the storage site.

A number of modules will be installed at three specifically chosen locations in the continental United States: one in Odessa, Texas (warm, dry climate); one in Bucks, Alabama (warm, wet climate); and one in Goose Creek, Illinois (temperate climate). Each site's proposed plant design will utilize a natural gas-fired CHP plant to provide the energy to run the DAC unit. The resulting combined system will capture more than 100,000 tonnes of CO_2 from the atmosphere (*after* accounting for the CO_2 produced by the CHP plant). This concept is referred to as DAC+, as it is able to accomplish all of these tasks from within a single facility. The Alabama site's results will be compared to those of a standard amine-based absorption system as a means of better highlighting the strength of GT's adsorption technology for at least one of the sites.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Project Value**
True Density @ STP	kg/m^3	2,300
Bulk Density	kg/m^3	500
Average Particle Diameter	mm	0.23
Particle Void Fraction	m^3/m^3	0.78
Packing Density	m^2/m^3	1,800
Solid Heat Capacity @ STP	kJ/kg-K	0.81
Crush Strength	kg$_f$	4
Thermal Conductivity	W/(m-K)	0.4
Adsorption		
Pressure	bar	1.0
Temperature	°C	25
Equilibrium Loading	g mol CO_2/kg	2.5
Heat of Adsorption	kJ/mol CO_2	85-95
CO_2 Adsorption Kinetics	mol/kg-min	0.043
Desorption		
Pressure	bar	1.0
Temperature	°C	100
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.05
Heat of Desorption	kJ/mol CO_2	85-95
CO_2 Desorption Kinetics	mol/kg-min	0.3
Proposed Module Design		
Flow Arrangement/Operation	—	Honeycomb Monolith
Air Feed Approach Velocity	m/sec	5
Space Velocity	hr^{-1}	120
Volumetric Productivity	mol$_{CO2}$/(hr-kg$_{sorbent}$)	2.7
CO_2 Recovery, Purity, and Pressure	% / % / bar	50/95/1.0
Adsorber Pressure Drop	bar	0.002
Degradation	% capacity fade/yr	5%

**Development in materials properties is prohibited within this project area of interest (AOI) and therefore project-derived changes to these numbers is out of scope and not anticipated.

A complete TEA and LCA is being performed as a part of this study. Preliminary capture cost estimates for the DAC+ carbon capture system installed with a CHP plant are shown in Table 2.

TABLE 2: DAC+ ECONOMICS

Economic Values	Units	Target Project Value
Cost of Carbon Captured	\$/tonne CO_2	90-150
Cost of Carbon Captured (Net Removal Basis)	\$/tonne CO_2	130-240
Capital Expenditures (annualized at 10%)	\$/tonne (net)	70-130
Operating Expenditures	\$/tonne (net)	60-110

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon (Net Removal Basis) – Projected cost of capture per mass of CO_2 under expected operating conditions for net removal from the atmosphere

Capital Expenditures – Projected capital expenditures (CAPEX) in dollars per tonne on a net removal basis. Cost estimates use annualized values at 10% of CAPEX.

Operating Expenditures – Projected operating expenditures in dollars per tonne on either a total or a net removal basis.

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is $ per tonne of CO_2 in CO_2-rich product and assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The GT DAC system employs a solid-sorbent system.

Sorbent Contaminant Resistance – Air borne contamination mitigated with filters.

Sorbent Attrition and Thermal/Hydrothermal Stability – Targeted lifetime for sorbent is three years.

Flue Gas Pretreatment Requirements – Not established yet.

Sorbent Make-Up Requirements – Replacement after capacity loss tolerance level exceeded.

Waste Streams Generated – Waste gases mostly water.

technology advantages

- Modular design.
- Enables carbon-negative fossil power generation and carbon-neutral synthetic fuels.
- Low pressure drops.
- Future-proof—different adsorbent materials can be slotted into the units, allowing future generations of adsorbents to be used with the design to reduce cost of future upgrades.
- High selectivity—can capture CO_2 at incoming concentrations as low as 400 parts per million (ppm).

R&D challenges

- Integrating DAC+ system with commercial host sites.
- Completing the detailed TEA and LCA for all three sites.

status

Process and equipment design for the host site in Alabama is underway. A comparative analysis of DAC+ and DAC combined with conventional capture from CHP unit flue gas is underway.

available reports/technical papers/presentations

Steutermann, M., “Scaleup and Site-Specific Engineering Design for Global Thermostat Direct Air Capture Technology.” Project Kickoff Meeting. Pittsburgh, PA. December 13, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12682&filename=Scaleup+and+Site-Specific+Engineering+Design+for+Global+Thermostat+Direct+Air+Capture+Technology.pptx.*

Transformational Sorbent-Based Process for Direct Air Capture

primary project goal

InnoSepra LLC is advancing an adsorption-based direct air capture (DAC) process. The overall goals of the project are to generate data to confirm that the process can provide significant cost and parasitic power savings compared to state-of-the-art DAC processes and to utilize process models to produce a conceptual design of a large-scale DAC system.

In Phase I, the technical and economic feasibility of the technology was demonstrated through laboratory testing, process modeling, and a preliminary techno-economic analysis (TEA). The Phase II objectives are to scale-up and test optimized materials (developed in a separate DOE-funded project) in structured form for CO_2 removal and moisture removal using semi-bench units in the laboratory; design, construct, and test a bench-scale unit at the National Carbon Capture Center (NCCC); and update the process model, process simulation, and TEA to predict performance and cost of commercial-scale systems.

technical goals

- Construction of semi-bench and bench-scale units capable of dehumidifying 10–250 standard cubic feet per minute (scfm) of air.
- Construction of semi-bench and bench-scale units capable of carbon dioxide (CO_2) capture tests for the CO_2 adsorption part of the process.
- Process data collection for the feed dehumidification and the CO_2 capture parts of the process.
- Installation and testing at NCCC, validating the process simulation model for the proposed process.
- Estimation of capital cost (CAPEX), operating cost (OPEX), and CO_2 capture cost for approximately 250-tonne-per-day (tpd) CO_2 capture from air.

technical content

The Phase I project was based on utilizing physical sorbents in particulate form for capturing CO_2 from the air and further upgrading it to purities needed for pipeline transport. In contrast to amine-based systems, the heats of adsorption of CO_2 on physical sorbents range between 30–40 kJ/mole of CO_2—about a fifth of the total energy needed for amine-based absorption systems. Even after adding the heat needed for vessel and sieve heating, and the sensible heat for heating CO_2, the total energy required is significantly lower than that for amine-based solvents and reactive sorbents. This can lead to significantly lower parasitic power consumption. InnoSepra discusses the use of physical sorbents for CO_2 capture from power plants. The sorbents used in the InnoSepra process have a much higher surface-to-volume ratio (greater than $1x10^6$ m^2/m^3) compared to structured packings used in absorption processes (less than 1,000 m^2/m^3) and membranes (250–5,000 m^2/m^3 for plate-and-frame, spiral-wound, and hollow fiber modules, respectively), which allows a five-foot tall adsorption bed to provide the same or better separation of CO_2 as a 200-foot tall absorption column.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Physical Sorbent-Based Process for DAC

participant:
InnoSepra LLC

project number:
SC0020740

predecessor projects:
N/A

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partners:
N/A

start date:
06.29.2020

percent complete:
40%

In the InnoSepra process, the CO_2 in ambient air, about 400 parts per million (ppm), is concentrated to a stream containing greater than 95% CO_2,which can be transported through a CO_2 pipeline for storage or enhanced oil recovery (EOR). DAC plants can be standalone plants or they can be part of CO_2 capture at a power plant and utilize the power from the plant for capture. This can be particularly advantageous during times when the power demand from the fossil-fuel-based power plant is low and the power prices are very low or even negative during high renewables penetration.

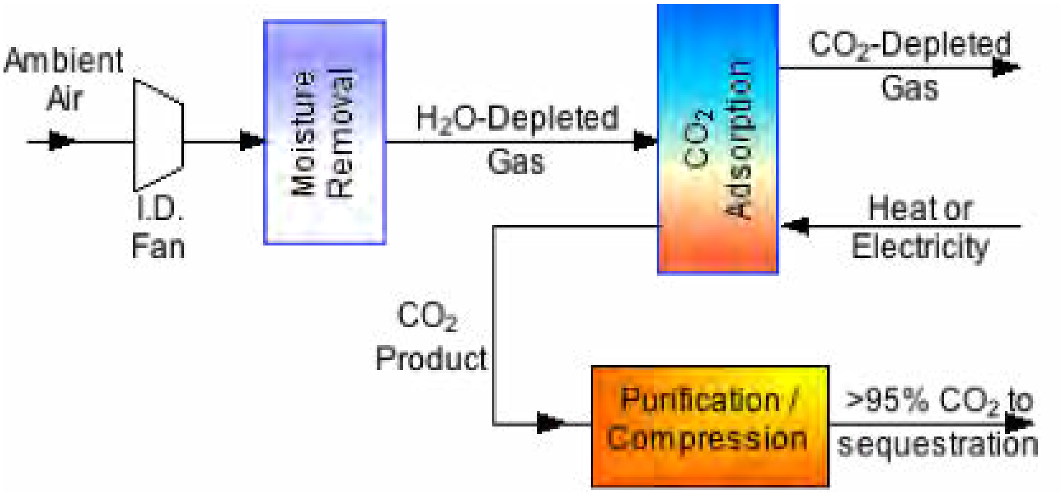

Figure 1. Process schematic for the InnoSepra process.

The process schematic in Figure 1 shows the proposed process for DAC. The pressure of ambient air is raised by 0.1–0.2 pounds per square inch (psi) in an induced draft (ID) fan and the compressed air is sent to a rotating bed moisture adsorption unit for removing moisture and a CO_2 adsorption unit in sequence. Because of the very large gas volumes involved with DAC, the system pressure drop for CO_2 capture needs to be minimized and structured sorbents are used in both stages for this to be accomplished. The pressure drop in each of these stages is expected to be less than 0.05 psi. Depending on the fabrication method, the costs of the structured sorbents are not significantly higher than the cost of particulate sorbents.

The purpose of the moisture adsorption system is to reduce the relative humidity of the feed gas to below 1% to minimize the moisture adsorption on the CO_2 sorbent. The rotating bed configuration for moisture removal is shown in Figure 2. The entire structure is housed inside a duct. The typical wheel depth is eight to 16 inches. Short bed height coupled with a large open area, greater than 75%, leads to a very low pressure drop. One rotation of the wheel takes six to 12 minutes, during which time the entire wheel undergoes adsorption (in the adsorption zone) and regeneration (in the regeneration zone). A rotating seal is used to separate the adsorption and regeneration zones. The wheel areas used for adsorption and desorption steps are nearly equal. For this dehumidification process, the adsorbent volumes needed are reduced by a factor of more than 10 compared to the particulate sorbents. Flue gas dehumidification using rotating wheel adsorbers provides very significant process intensification and is very important for DAC.

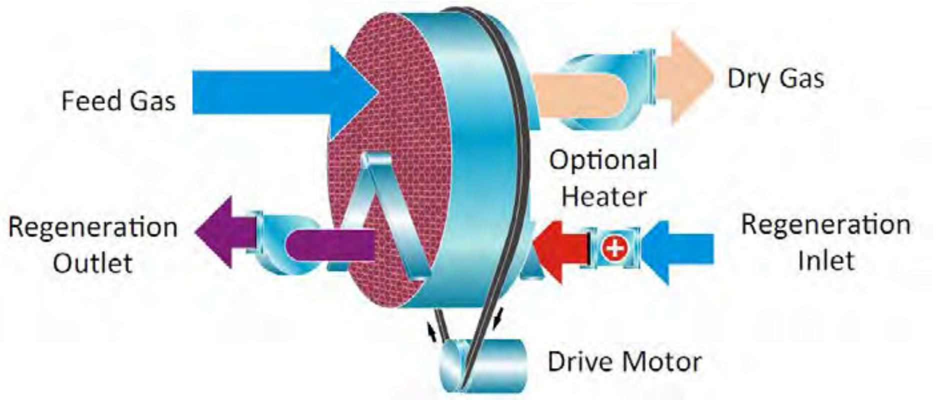

Figure 2. Rotating wheel dryer for feed dehumidification.

The moisture-depleted gas is sent to a CO_2 adsorber containing a sorbent that has a high CO_2 capacity at low CO_2 partial pressures. These sorbents can be thermally regenerated to produce a first CO_2 product stream that can be further purified and compressed to produce a CO_2 stream suitable for pipeline transport (Figure 1). The process operates continuously and does not require any switching valves, unlike the fixed bed adsorption processes.

The CO_2 adsorber is a rotating bed (similar to that in Figure 2) or a parallel passage contactor. Again, the pressure drop in this step is less than 0.03 psi. The regeneration of CO_2 sorbents is done at 100–110°C and typically requires low pressure steam. Where possible, the steam for regeneration is generated by solar heating and is stored during non-daylight hours. The dry, CO_2-product stream is further concentrated to a purity (greater than 95% CO_2) suitable for pipeline transport in another stage. If the DAC system is sited at a power plant, synergies between post-combustion capture and DAC can be utilized to significantly reduce the cost of CO_2 capture using DAC. The power plant can be utilized to provide steam and electrical power needed for capture.

The second key element of the proposed system is the adsorption of CO_2 on structured sorbents with very high capacities at low CO_2 partial pressures. Whereas typical physical sorbents have CO_2 capacities below 1 wt% for typical CO_2 concentrations in air, the InnoSepra materials have a CO_2 capacity of more than 4.0 wt% for 400-ppm CO_2 in air. These materials also have low heats of adsorption (less than 42 kJ/mol of CO_2). These high CO_2 capacities and low heats of adsorption significantly reduce the regeneration energy needed for DAC. The regeneration energy requirement for this system is significantly lower compared to other DAC technologies. The use of structured sorbents for moisture removal and CO_2 capture allows the equipment to be shop-fabricated and field-assembled, significantly reducing fabrication and transportation costs.

The third key element of the proposed system is the regeneration of the CO_2-containing sorbent to produce a pipeline-quality CO_2 product in two stages. The final CO_2 product is compressed to a pressure of approximately 2,200 pounds per square inch gauge (psig) for pipeline transport. A cooling water stream is heated to 50–70°C in the CO_2 compressor train, utilizing the CO_2 heat of compression, and provides some of the process heating needs. The estimated energy required for the CO_2 capture for an air feed containing 400-ppm CO_2 is given in Table 1. This assumes feed compression to 0.1 psig, a heat of adsorption of 42 kJ/mol of CO_2, and a net adsorption capacity of 3.5 wt%. The energy consumption to capture CO_2 at a pressure of 1 bara is approximately 550 kJ/mol of CO_2 (4.6 GJ/tonne). This number is significantly lower than the 1,000 kJ/mol of CO_2 (less than 8.5 kJ/mol) needed for amine-based sorbents for DAC.

TABLE 1: ENERGY REQUIRED FOR CO_2 AND MOISTURE REMOVAL SECTIONS

Heat of Desorption	1.0 GJ/tonne of CO_2
Sensible Heat for CO_2	0.1 GJ/tonne of CO_2
Sensible Heat for the Sorbent	3.0 GJ/tonne of CO_2
Dehydration Energy	0.1 GJ/tonne of CO_2
Mechanical Energy	0.4 GJ/tonne of CO_2
TOTAL	**4.6 GJ/tonne of CO_2**

TABLE 2: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,600	1,600
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	<0.1	<0.01
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1e+8	1e+8
Solid Heat Capacity @ STP	kJ/kg-K	1.00	1.00
Crush Strength	kg_f	>10	>10
Attrition Index	-	<0.01%	<0.01%
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	$/kg	15	10
Adsorption			
Pressure	bar	1.01	1.005
Temperature	°C	25-35	25-35
Equilibrium Loading	g mol CO_2/kg	0.9	1.2
Heat of Adsorption	kJ/mol CO_2	44	44
CO_2 Adsorption Kinetics	gmol/time	0.2	0.5
Desorption			
Pressure	bar	0.2-1.0	0.2-1.0
Temperature	°C	100-150	90-105
Equilibrium CO_2 Loading	g mol CO_2/kg	0.2	0.1
Heat of Desorption	kJ/mol CO_2	44	44
CO_2 Desorption Kinetics	gmol/time	0.4	0.6
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr^{-1}	—	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— —	—
Adsorber Pressure Drop	bar	—	
Degradation	% capacity fade/cycle	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is the market price of material, if applicable; “Target” is the estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

	Composition						
Pressure	vol%					ppmv	
14.7 psia	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physical.

Sorbent Contaminant Resistance – No impact of oxygen and moisture in feed air, acid gas impurities are not relevant to DAC.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – At least five-year life before any make-up is needed.

Waste Streams Generated – N/A.

Proposed Module Design – N/A.

TABLE 3: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	175-200	150-175
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	100-115	80-100
Operating Expenditures	\$/tonne CO_2	75-85	70-75

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – No U.S. Department of Energy (DOE) reference case for DAC.

Scale of Validation of Technology Used in TEA – Lab-scale.

Qualifying Information or Assumptions – N/A.

technology advantages

- Very low pressure drops (typically one-fifth to one-tenth used for particulate sorbents for the same flow rate).
- Not subject to fluidization constraints or attrition issues.
- Very small effective particle size (less than 80 µm), leading to very short mass transfer zones.
- Can process significantly higher flows for a given bed volume.
- The materials are low cost and can be produced in very large quantities fairly quickly.
- Can be fabricated with virtually any sorbent.
- Equipment is commercially available up to 10 feet in diameter.

R&D challenges

- Identifying pathways for materials fabrication at large scale and further process scale-up.

status

InnoSepra LLC is currently working on the design, engineering, and manufacturing of the 250-tpd DAC system. Model development for the DAC system and process simulation are also going on concurrently. Work has been initiated on a bench-scale system for testing at NCCC.

available reports/technical papers/presentations

Ravi Jain, Norberto Lemcoff, “Transformational Sorbent-Based Process for Direct Air Capture,” Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12451&filename=Transformational+Sorbent-Based+Process+for+Direct+Air+Capture.pdf*.

Dual Function Materials for Direct Air Capture of CO_2

primary project goal

Susteon Inc. is teaming with Columbia University, Applied Catalysts, and Kiewit Engineering to advance the development of a “reactive” direct air capture (DAC) process that is capable of capturing and converting carbon dioxide (CO_2) from air into valuable products. The reactive DAC process involves selective chemisorption of CO_2, followed by sorbent regeneration through reversible desorption or, optionally, catalytic conversion of adsorbed CO_2 into methane (CH_4; also referred to as renewable natural gas [RNG]), using waste or renewable hydrogen (H_2).

In Phase I of this Small Business Innovation Research (SBIR) project, the research team optimized existing dual-function materials (DFMs), originally developed for treating flue gas from large point sources, for application in removing CO_2 from air. The DFM exhibited a high CO_2 adsorption capacity and capture kinetics in ambient air. The technical and economic feasibility of the “reactive” capture DAC process was demonstrated successfully in Phase I.

Phase II is focused on further optimizing the DFMs and process cycle; developing a high-fidelity bench-scale (1 kg/day) prototype unit to perform parametric and long-term testing; optimizing DFM on the selected support structure to achieve maximum CO_2 adsorption capacity, low pressure drop, and conversion into methane; developing a process model to accurately represent the process; and performing and refining the techno-economic assessment (TEA) obtained in Phase I to evaluate the commercial potential of the process.

technical goals

- Develop optimum DFM washcoat formulation on commercial monolith support through lab- and bench-scale testing.
- Develop an efficient method of heating the DFM layer on the monolith using Joule heating.
- Develop a commercial manufacturing process for DFM structures by working with a commercial catalyst manufacturer.
- Design and build a bench-scale unit capable of 1.0 kg/day of CO_2 capture.
- Conduct parametric testing in the bench-scale unit to determine optimum DAC-DFM process conditions for CO_2 adsorption, RNG production, and optimum process cycle design.
- Conduct long-term testing to establish DFM aging and performance degradation.
- Refine and validate the current process model using bench-scale data to develop a high-level process design for a pilot-scale (50 kg CO_2/day) system scale-up and testing in the next phase.
- Perform a TEA and LCA.

technical content

DAC of CO_2 is a promising technology that can potentially contribute to mitigation of CO_2 emissions at scale. DAC technology can be also used to provide sustainable CO_2 as feedstock for CO_2 conversion technologies to produce

program area:

Carbon Dioxide Removal

ending scale:

Bench Scale

application:

Direct Air Capture

key technology:

Sorbents

project focus:

Dual Function Materials for Capture and Conversion of CO_2 into Methane

participant:

Susteon Inc.

project number:

SC0020795

predecessor projects:

N/A

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principal investigator:

Raghubir Gupta
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partners:

Columbia University; Kiewit Engineering Group Inc.

start date:

06.29.2020

percent complete:

47%

synthetic fuels, chemicals, and construction materials. In this project, Susteon is advancing the development of a “reactive” DAC system that is capable of capturing, as well converting, CO_2 from air into valuable products.

In Phase I of this project, Susteon successfully demonstrated this process-intensified reactive DAC process using DFMs for capture of CO_2 from air and its subsequent conversion into CH_4 using renewable/waste hydrogen for regeneration. The DFM porous solid material, consisting of a novel combination of an adsorbent and a catalyst, has shown high CO_2 capacity under DAC conditions, and even greater capacity in the presence of atmospheric moisture, in laboratory experiments. Regeneration can be achieved using mild temperatures (200–300°C), minimizing the temperature difference between chemisorption and sorbent regeneration and mitigating the need for heating and cooling of the reactor beds, which are typically needed in most adsorption-based processes. The “green” CH_4 formed in this process can be sold as RNG, which qualifies for various carbon credits and incentives, similar to biogas, landfill gas, etc. This reactive DAC process is designed to intensify both the capture and utilization of atmospheric CO_2, creating a platform technology for production of a variety of green hydrocarbon products from air (i.e., CH_4, methanol, dimethyl ether, olefins, diesel, aviation fuel, etc.). As shown in Figure 1, air is fed into an adsorption reactor containing DFM, which rapidly captures CO_2 from ambient air. Once the bed is saturated with CO_2, it is heated to about 170°C and regenerated with an H_2-containing gas stream to directly react CO_2 to produce CH_4 using the Sabatier reaction ($CO_2 + 4H_2 = CH_4 + 2H_2O$). This project is aimed at demonstrating the production of RNG at a cost comparable or better than the current RNG prices in California with low-carbon fuel standards (~$15/MM British thermal units [Btu]), creating a business opportunity for further development and deployment of this DAC technology.

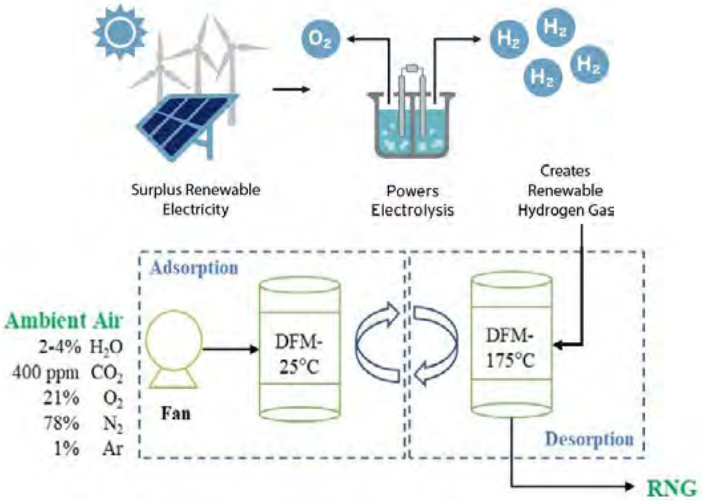

Figure 1: Block flow diagram for the overall DAC-DFM process using renewable H_2.

In Phase I, working with research institute partner Columbia University, Susteon identified, synthesized, and tested a ruthenium (Ru)-promoted sodium oxide dispersed on alumina as the DFM for this process. DFM optimization in Phase I led to identification of 0.25% Ru + 10% Na_2O supported on a high-surface area Al_2O_3 DFM, which exhibited a high CO_2 adsorption capacity and capture kinetics in ambient air. The extent of CO_2 capture (% removal of 400 parts per million [ppm] CO_2 in air) was significantly higher in the presence of atmospheric moisture (relative humidity in air), unlike physical sorbents like zeolites, aluminas, metal organic frameworks (MOFs), and even amine-based CO_2 capture sorbents. This DFM also showed a very fast mass transfer rate during adsorption and desorption/methanation without any noticeable aging/degradation. The preliminary TEA of the DFM-based DAC system (Figure 2) with 1 tonne CO_2/day basis indicated a combined power and heat requirement of 2,300 kWh/tonne CO_2, which involves (a) CO_2 capture under ambient conditions without needing to heat or pressurize air followed by (b) heating the DFM for initiating methanation to 120–200°C. The methanation reaction being significantly exothermic (-164 kJ/mol) creates opportunities to utilize and integrate this heat to further lower the overall energy need. The DFM material is used on a structured support (e.g., cordierite monoliths used in automobile catalytic converters) to minimize pressure drop.

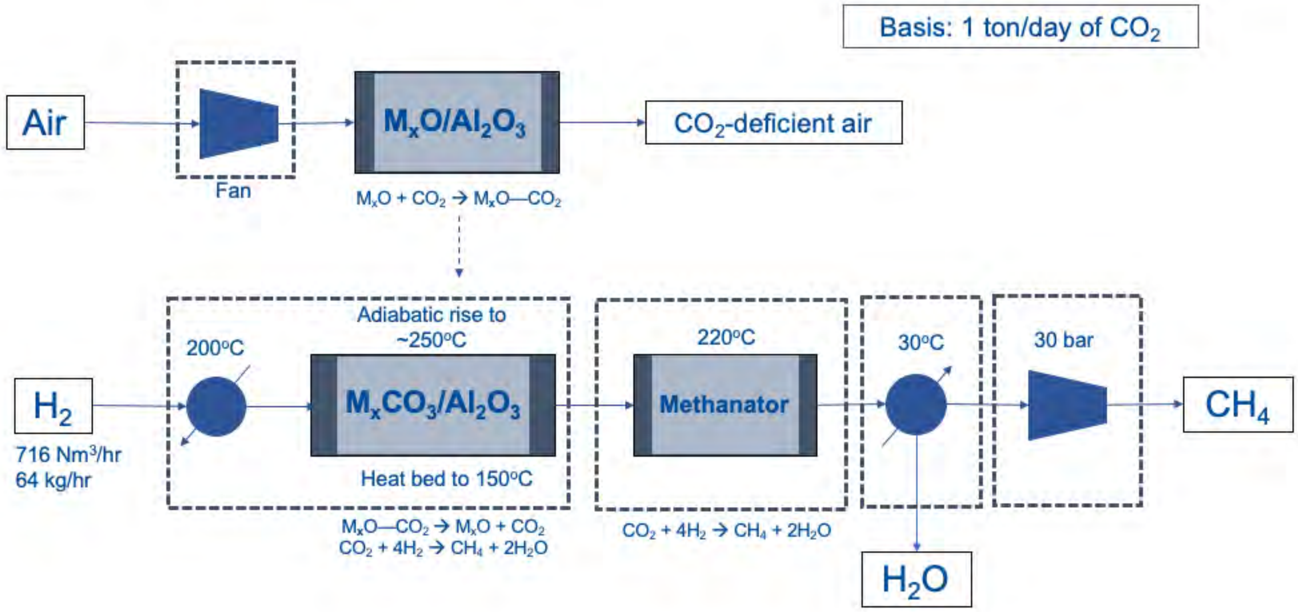

Figure 2: DAC-DFM with CO_2 capture at ambient conditions (25°C).

The Phase II project is aimed at further optimizing the DFMs and process cycle and building a high-fidelity bench-scale prototype unit to demonstrate this process and obtain engineering data needed for a pilot system design in a follow-on phase. DFM optimization focuses on the formulation and dispersion of DFM on the commercially available structured supports to achieve maximum DFM stability, CO_2 adsorption capacity, and rapid kinetics of CO_2 adsorption and methanation reactions. This work involves further reducing the Ru loading to lower overall cost of CO_2 capture. A novel Joule heating method is being integrated in the structured support to selectively heat the DFM layer between adsorption and regeneration steps. Bench-scale testing is being conducted to determine DFM process conditions that yield the fastest CO_2 adsorption rate, highest CO_2 capacity, maximum CH_4 production, and lowest-energy consumption for reactive DAC. The process model is validated using lab- and bench-scale data and employed to develop a high-level process design for a 50-kg/day engineering-scale reactive DAC system, as well as techno-economic analysis (TEA) and life cycle analysis (LCA) studies on a commercial-scale system. Lab- and bench-scale test results are used to further refine the process model developed in Phase II.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Both chemisorption and physisorption occur during the adsorption step.

Sorbent Contaminant Resistance – To be determined.

Sorbent Attrition and Thermal/Hydrothermal Stability – To be determined.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – To be determined.

Waste Streams Generated – N/A.

Process Design Concept – See Figure 1 for block flow diagram and Figure 2 for more detailed DAC-DFM reaction scheme.

Proposed Module Design – To be determined.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	312	205
Produced RNG	tonne/day	18.2	32.4
Net Cost of Carbon Captured[i]	\$/tonne CO_2	197	0
Capital Expenditures	\$/tonne CO_2	187	86.1
Operating Expenditures	\$/tonne CO_2	125	115

[i] Projected cost of capture less revenue from RNG sales based on the current RNG price of \$15/MMBtu (including carbon credits), and a renewable hydrogen price of \$2/MMBtu.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Net Cost of Carbon Captured – Projected cost of capture less revenue from RNG sales per mass of CO_2

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The economic values in Table 2 result from a process model on a 100 tonne/day captured CO_2 basis. The model developed in Aspen Plus was used to generate process material and energy balances, equipment sizing, and costs with the following assumptions:

- 25°C ambient temperature.
- 101.325 kPa ambient pressure.
- 60% relative humidity air.
- 1 kPa pressure drop in shell and tube heat exchangers.
- Compressor/blower specification: Polytropic with 70% efficiency and 90% drive motor efficiency.
- 10°C approach to cooling water on aftercooler heat exchanger.

- RGibbs reactor model for all reactions, including adsorption, desorption, and methanation.

Scale of Validation of Technology Used in TEA – The DAC economic values in Table 2 result from analysis of fundamental lab-scale data gathered at Technology Readiness Level (TRL) 3, implying a significant level of uncertainty in the process design and cost for a commercial system. This analysis is undertaken in the early stages of the technology development cycle to establish the feasibility of this novel technology with respect to technical soundness, operational flexibility, and economic viability.

Qualifying Information or Assumptions – Initial preliminary TEA results are based on the current RNG price of \$15/MMBtu (including carbon credits), and hydrogen price of \$2/MMBtu.

technology advantages

- Provides a saleable product from CO_2 with a strong market demand; for this project, it is RNG, which is in heavy demand to meet the low-carbon standards for CH_4 and power.
- Eliminates the need for CO_2 disposition infrastructure; compression, pipelines, storage sites, and long-term monitoring as CO_2 is directly converted into a saleable product, which can be distributed in existing natural gas infrastructure.
- Provides a platform for delivering renewable methane (RNG) from atmospheric CO_2 (Power-to-Gas) for downstream utilization to produce “green” hydrocarbons like methanol, Fischer-Tropsch fuels, olefins, etc. This could be accomplished by incorporating appropriate catalysts during the regeneration.
- Provides a market mechanism by utilizing current subsidies/incentives for low/negative carbon products (so called “Green Premiums”) for offsetting the cost of DAC by revenue generated by selling the products manufactured from CO_2.

R&D challenges

- Designing an efficient process cycle for adsorption, heating, desorption, methanation, and cooling to maximize capital productivity and minimize the overall capital expenses (CAPEX) and operating expenses (OPEX) for the technology.

status

Susteon is currently working on a process model to predict key performance parameters involved in their DAC process, such as overall capture efficiency, energy consumption, CH_4 yield, and DFM degradation rates. Additionally, the bench-scale test system design, equipment sizing, and procurement are also currently being completed.

available reports/technical papers/presentations

Raghubir Gupta, “Dual Function Materials for Direct Air Capture of CO_2,” Phase II Project kickoff meeting presentation, Pittsburgh, PA, September 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12122&filename=Dual+Function+Materials+for+Direct+Air+Capture+of+CO2.pdf*.

Demonstration of Direct Air Capture of CO_2 with Building Air-Handling Equipment

primary project goal

Oak Ridge National Laboratory (ORNL) is evaluating the feasibility of integrating carbon capture technologies with existing heating, ventilation, and air conditioning (HVAC) systems in buildings to remove carbon dioxide (CO_2) directly from ventilated air streams. The use of existing air handling infrastructure can enable the deployment of distributed direct air capture (DAC) systems that are modular and scalable. The project is assessing specific types of buildings and associated equipment in order to identify the major opportunities and challenges associated with DAC incorporation into representative building HVAC systems. To execute this multi-faceted project, an integrated project team from ORNL's Energy and Transportation Science Division is tasked with applying capabilities and technologies associated with HVAC equipment, advanced materials, and system integration.

technical goals

- Perform a preliminary assessment of utilizing existing building equipment infrastructure for DAC.
- Characterize adsorbent materials and modules for this application.
- Assess various approaches for regeneration of sorbents.
- Evaluate system integration options and assess the impact on equipment performance due to additional power requirements.
- Perform a techno-economic assessment (TEA) of DAC in buildings and conduct a feasibility analysis based on building processes and occupant comfort.

technical content

Centralized DAC is an expensive technology requiring logistics support, large-scale air-moving technology, and sorbent regeneration capability where the levelized costs are in the range of 94–232 $USD/tonne-$CO_2$, as shown in Figure 1. A distributed approach may be more feasible and lead to lower-cost DAC. There are more than 120 million buildings across the United States (114 million residential and 6 million commercial). Existing building HVAC equipment is capable of moving large amounts of air using installed blowers and fans. The air-handling infrastructure may be able to be retrofitted with a distributed DAC system. The approach to this technology is to develop a highly modular and scalable technology for CO_2 capture, enabling distributed deployment in residential and commercial HVAC systems with minimal capital and operational costs.

The primary objectives of this project are to conduct a preliminary assessment of HVAC systems to ascertain what kind of system design is needed, perform a demonstration of DAC using existing building equipment, and quantify the techno-economic impact of this distributed approach to DAC technology.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Building HVAC Retrofit with DAC System

participant:
Oak Ridge National Laboratory (ORNL)

project number:
FWP-FEAA156

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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partners:
N/A

start date:
08.01.2020

percent complete:
71%

Figure 1: Centralized DAC technology.

Preliminary assessment of the technology regeneration approaches reveals that the building exhaust air is 30–35°C. Condenser heat approximately 50°C can be used to pre-heat a liquid sorbent for regeneration. The onsite gas-fired furnace can be modulated to provide ancillary heat for sorbent regeneration at approximately 100°C. The form of the sorbent can be chosen to minimize pressure drop while keeping a high surface area. The adsorbent module consists of modules with several CO_2 filters in series in order to achieve a large enough CO_2 capture breakthrough period. The test plan for adsorbent materials is to consider both physisorption and chemisorption materials. Physisorption materials have lower CO_2 capacity, but are easily regenerated. Chemisorption materials have higher CO_2 capture capacity, but also need higher temperatures for sorbent regeneration.

technology advantages

- Existing HVAC equipment may be used, lowering both capital and operating costs for DAC technology.

R&D challenges

- Developing a highly modular and scalable technology for CO_2 capture for distributed application.

status

The ORNL project team is in several discussions with industrial original equipment manufacturers to assess the HVAC technology and the potential for incorporating a DAC technology. The design phase of the DAC module is currently under way, along with evaluation of potential adsorbent materials.

available reports/technical papers/presentations

Kashif Nawaz, “Demonstration of Direct Air Capture (DAC) of CO_2 with Building Air Handling Equipment,” DAC Kickoff Meeting, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Nawaz.pdf*.

Demonstration of a Continuous-Motion Direct Air Capture System

primary project goal

Global Thermostat LLC (Global), in partnership with Zero Carbon Partners, VADA LLC, Georgia Institute of Technology, and the National Renewable Energy Lab, will develop a continuous motion direct air capture (DAC) system that will capture carbon dioxide (CO_2) from the air through an adsorption process and produce a greater than 95% purity CO_2 product. The process employs honeycomb monolith contactors with a solid amine sorbent incorporated into the pores of the monolith, resulting in high CO_2 adsorption capacities at very low CO_2 partial pressures. The project team is designing and validating the mechanical components of the system and completing detailed engineering and sizing of the process equipment. In parallel, a phenomenological flow model and a systems-level Aspen model is being developed to refine process step development, monolith lifetime, and key performance tradeoffs. Global is leveraging the phenomenological model to inform experimental work while assessing the impacts on sorbent lifetime. The process equipment is being fabricated, delivered, and integrated with the mechanical system to form an integrated DAC system. The prototype DAC unit will be commissioned and operated at the Global Thermostat Technology Center to collect onstream data that will inform the techno-economic and life cycle analyses (TEAs and LCAs).

technical goals

- Develop the mechanical component and process equipment prototype engineering design.
- Develop a phenomenological flow model and a systems-level Aspen model that will refine process step development, estimate monolith lifetime, and key performance tradeoffs. Validation of models from experimental data will be used to supplement the basic engineering design for component capital expenditure (CAPEX) estimation and scaling analysis.
- Perform initial TEA and LCA to evaluate purge-step tradeoffs, cost sensitivity to key parameters, and scale-up versus scale-out cost projections.
- Generate operational data from the DAC prototype, including a prolonged period of continuous operation, to feed into and refine the Aspen model to inform the prescreening TEA and LCA deliverables.
- Following the process conditions optimization, the unit will be operated continuously for one month to collect onstream data and demonstrate operability and reliability.

technical content

A primary challenge for DAC is low-cost, high-efficiency air contact. The Global DAC process employs relatively shallow honeycomb monolith contactors (~15 cm deep) that permit low pressure drops (100s of Pa) at gas approach velocities of 3–5 meters per second (m s^{-1}) while still maintaining a high geometric surface area per unit volume (Figure 1). This approach minimizes costs for gas processing by allowing the use of draft fans for gas movement upstream of the capture process.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Honeycomb Contactor with Amine-Based Sorbent for DAC

participant:
Global Thermostat LLC

project number:
FE0031957

predecessor projects:
N/A

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eric.ping@globalthermostat.com

partners:
Georgia Institute of Technology; VADA LLC; Zero Carbon Partners LLC

start date:
10.01.2020

percent complete:
44%

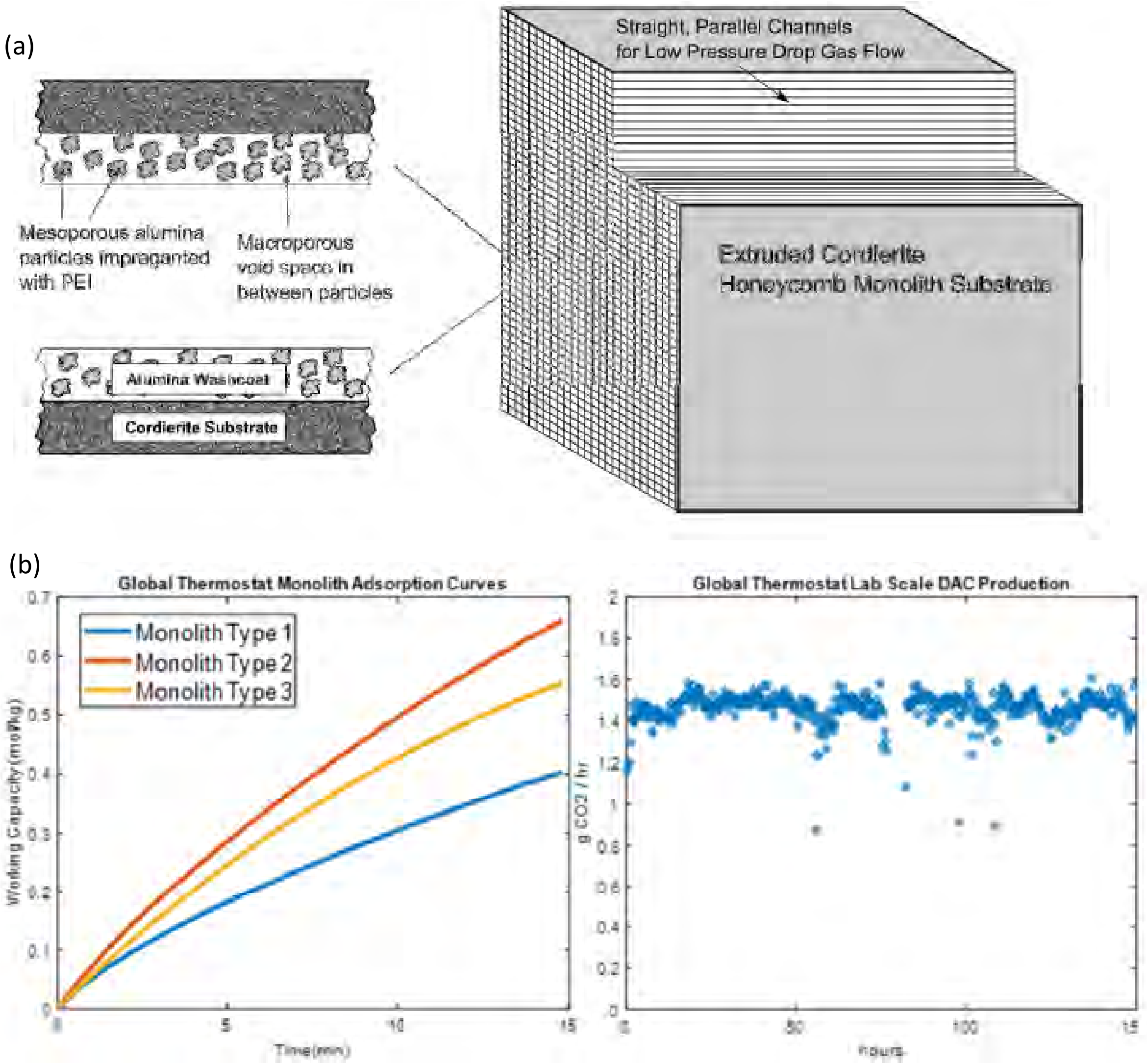

Figure 1: (a) Schematic of monolith used in the Global process; (b) 15-minute DAC working capacities for Global monoliths developed.

Monolith contactors are already made on a commercial scale for numerous applications, and the technology to wash coat them with porous oxide films is mature. Global has active Joint Development Agreements (JDAs) with three global monolith manufacturers that have resulted in several production generations of advanced DAC material technology. The adsorbent itself is critical to the efficacy of the process, as it sets the productivity levels and regeneration requirements. Global has worked with Georgia Tech for several years on sorbents specifically designed for DAC. The current sorbent material is low molecular weight (~800 Dalton), highly branched poly(ethyleneimine) (PEI) that is incorporated into pores within a monolith. This allows for high volumetric amine loadings (i.e., amine sites/adsorbent volume). Solid amine adsorbents interact with CO_2 via a chemisorptive mechanism, resulting in high CO_2 adsorption capacities at very low CO_2 partial pressures and high selectivity to CO_2 over other components in air, including water. It is well established that the presence of humidity in air improves the efficiency of the adsorbent. Working capacities up to approximately 0.65 mol CO_2 per kg sorbent have been demonstrated under the standard Global adsorption process conditions of 5 m s^{-1} air approach velocity and a 15-minute duration (Figure 1b).

A drawback of the current PEI sorbent is a limited lifetime, primarily due to oxidation and polymer leaching. Global has done extensive prior research in both of these areas to establish lifetime targets. Figure 1b shows cyclic onstream data at laboratory scale for approximately 150 continuous hours of operation. PEI leaching rates and oxidation rates have been measured and it is estimated that the sorbent can maintain 80% of its capacity over approximately 100,000 cycles.

Desorption of CO_2 is performed by a temperature swing delivered by condensation of saturated steam directly onto the monolith surface, raising the temperature to approximately 70–100°C. Steps are performed before and after this to maintain sorbent lifetime and achieve high CO_2 purity. The core sequence of the Global regeneration process cycle is as follows:

1. Reduction in O_2 concentration surrounding the monolith.
2. Direct contact condensation of steam to heat the monolith and desorb CO_2.
3. Cooling of the monolith by evaporation of condensed water on its surface.

Internal heat integration may be performed by recycling the stream, resulting from Step 3 and including it in Step 1. In the current first-generation Global batch process, Step 1 and Step 3 are performed using vacuum. In the second-generation continuous process described here, these steps are performed with inert gas or a recycled product CO_2 stream. Critically, CO_2 is being neither adsorbed nor desorbed in Step 1 or Step 3, so minimizing their cumulative step times is important for maximizing productivity. Step 3 is conducted at constant pressure and CO_2 is removed as it is evolved by a vacuum pump or blower. This approach produces a steam/CO_2 mixture that, after passing through a condenser/separator, gives a 95+% CO_2 product.

technology advantages

- Rapid cycles (less than 20 minutes) enabled by monolith contactor (adsorption) and steam regeneration (desorption); reduced amortized CAPEX.
- High capital utilization efficiency (improved CAPEX) while maintaining low pressure drop, improved operation expenses (OPEX) via panel movement.
- High uptakes enabled by amine dense sorbent (improved CAPEX and OPEX).

R&D challenges

- Physical movement of large components can be mechanically challenging, particularly in a batch process (start/stop).
- Maintaining adequate sorbent life over many cycles.
- Requires careful consideration of movement and sealing methodologies to maximize adsorbent lifetime.

status

Global Thermostat has developed computational fluid dynamics (CFD) models to understand airflow uniformity and air movement efficiency schemes. Process development Aspen Model has also been developed to understand the scalable model to evaluate costs at both large and pilot scale, utilities for steam generation and cooling water, and CO_2 compression costs. Monolith cooling has been proposed to be carried out with nitrogen instead of using vacuum and work is continuing to understand the tradeoffs with nitrogen purity and how this affects OPEX, CAPEX, sorbent lifetime, etc.

available reports/technical papers/presentations

Eric W. Ping, “Demonstration of a Continuous Motion Direct Air Capture System,” Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Ping.pdf*.

Miles Sakwa-Novak, “Demonstration of a Continuous Motion Direct Air Capture System,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Novak.pdf*

Direct Air Capture Using Novel Structured Adsorbents

primary project goal

Electricore Inc. is advancing a direct air capture (DAC) technology that combines a vacuum-temperature swing carbon dioxide (CO_2) adsorption process with structured adsorbent beds (SABs). The process employs Svante's novel solid sorbent laminate filter technology integrated with Climeworks' DAC technology in which CO_2 from air is chemically bound to a solid sorbent material and the sorbent is regenerated using vacuum- and temperature-swing desorption. The objective is to advance DAC technology and reduce capture costs of CO_2 from air by accelerating cycle times through the use of structured adsorbent beds.

technical goals

- Design, build, and operate a 30-kg/day integrated field test unit capable of producing a concentrated CO_2 stream of at least 95% purity.
- Conduct a 12-month field test of the DAC system to capture operational data on the novel process and material combination under real conditions.
- Perform a full characterization of first-, second-, and third-generation sorbent materials after at least 1,000 cycles of operation, with a goal of understanding failure modes to increase lifetime. The different sorbent generations have the goal of optimizing the sorbent structure geometry, reducing the amount of water uptake during adsorption, and improving CO_2 uptake.
- Use test data to advise techno-economic and life cycle assessments of the technology.
- The project will validate current state-of-the-art DAC systems and sorbent materials, and will achieve cost reductions through the use of advanced sorbents and energy optimization realized via reduced pressure drop in sorbent beds.

technical content

This project, led by Electricore, combines Climeworks' DAC process technology with Svante's SAB technology, and is being demonstrated at a test facility in California. Climeworks' DAC process technology adsorbs CO_2 from air on a solid adsorbent encased in a collector, and then regenerates using vacuum- and temperature-swing desorption (Figure 1). During adsorption, air is drawn into the collector with a fan. Carbon dioxide is captured on the surface of a selective sorbent, or "filter," that sits inside the collectors. Once saturated with CO_2, the filter is heated (using a low-grade heat energy source) to ~100°C. The CO_2 then releases from the filter and this continuous cycle begins again. In a standard Climeworks collector, sorbent is contained as a packed bed of particles, arranged in a patented geometry to minimize pressure drop in adsorption and heat demand in desorption.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent Bed Process for DAC

participant:
Electricore Inc.

project number:
FE0031959

predecessor projects:
N/A

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partners:
Climeworks; Svante Inc.

start date:
10.01.2020

percent complete:
40%

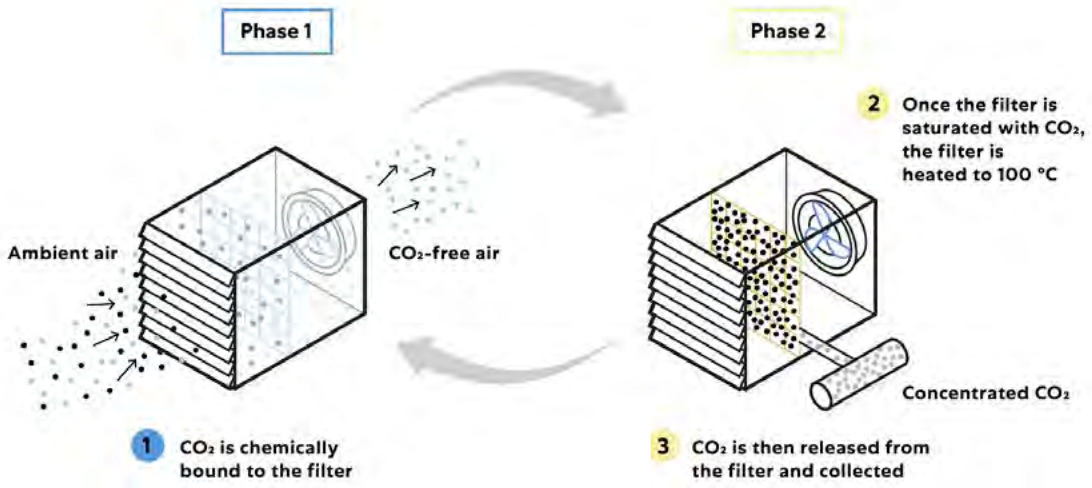


Figure 1: Schematic representation of Climeworks' adsorption and temperature-vacuum swing desorption processes for DAC.

Climeworks plants consist of modular CO_2 collectors. At full-scale, these modular collectors can be seen in Figure 2 at Orca, the world's largest DAC and storage plant, commissioned in Iceland in 2021 and operated with geothermal energy. The modular concept is scalable through "numbering-up." Collectors are designed for mass-production, enabling deployment on the large scale required for climate change mitigation.

Figure 2: Climeworks' Orca plant, the world's largest direct air capture and storage plant, commissioned in Iceland in September 2021, with a capture capacity of up to 4,000 t_{CO2}/year.

The project team's approach is to construct, operate, and test an integrated DAC system, combining Climeworks' contactor with Svante's novel solid sorbent laminate filter (Figure 3) under real conditions. Svante's sorbent technology consists of a patented architecture of structured adsorbent laminate (spaced sheets), containing tailor-made nanomaterials (solid adsorbents) with very high storage capacity for CO_2. This geometry enables very fast CO_2 uptake kinetics without incurring high pressure drops nor significant parasitic thermal mass, which keeps energy demand low.

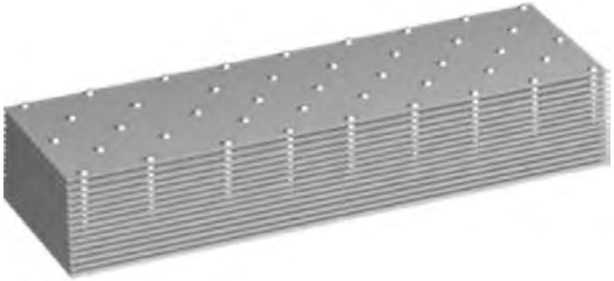


Figure 3: Svante's structured adsorbent bed structure.

Previously verified to Technology Readiness Level (TRL) 4 in the laboratory, performance targets for the combination of Climeworks' DAC process with Svante's structured adsorbent structure (Figure 4) will be validated in the field at a test facility built in California. Three generations of sorbent-structure combinations are being developed and tested to improve upon current performance. The sorbent filter lifetime is estimated at several thousand cycles (approximately two to three years); process parametric testing as well as durability studies are being undertaken to study this lifetime. The team will extrapolate collected data to estimate performance for a one-million-tonne-per-year plant and beyond, to confirm cost targets and to advise techno-economic and life cycle assessments of the DAC technology. Climeworks' collectors filled with novel solid sorbent materials produced by Svante enable an efficient adsorption-desorption process, allowing CO_2 extraction from diluted gas streams (such as air) at minimal energy demand, which is vital for implementation.

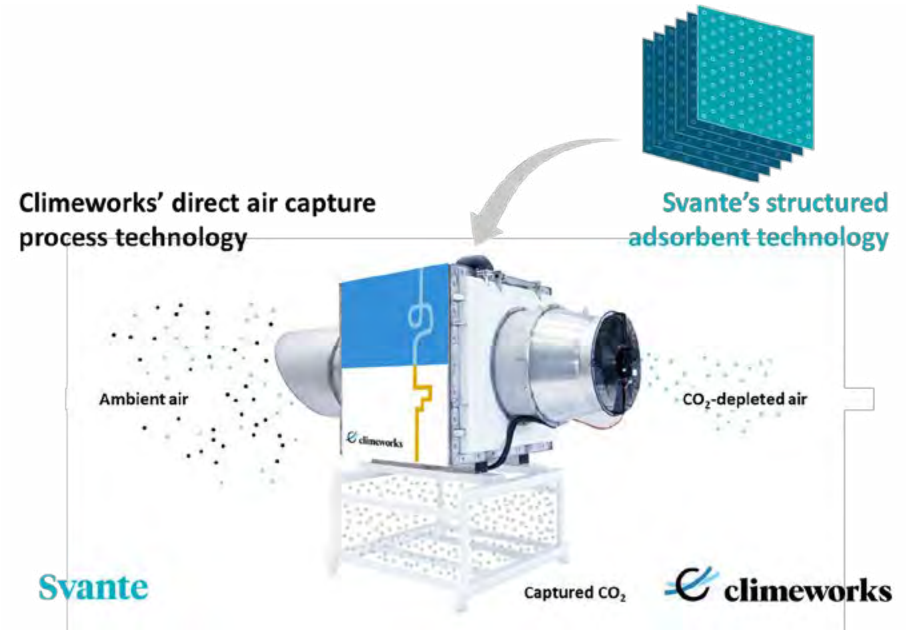


Figure 4: Climeworks' DAC technology with Svante's structured adsorbent technology.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current* R&D Value	Target R&D Value
True Density @ STP	$kg_{laminate}/m^3{}_{bed}$	100-270	80-150
Bulk Density	kg/m^3	N/A	N/A
Average Particle Diameter	mm (laminate thickness)	0.24-0.28	0.24-0.36
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density (wetted sheet area/bed volume)	m^2/m^3	1700-3000	1000-1700
Solid Heat Capacity @ STP	kJ/kg-K	1.4	1.4
Crush Strength	kg_f	N/A	N/A

Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	0.14-0.18	0.14-0.18
Adsorption			
Pressure	bar	ambient	ambient
Temperature	°C	ambient	ambient
Equilibrium Loading	g mol CO_2/kg	>1	>1
Heat of Adsorption	kJ/mol CO_2	70-80	70-80
CO_2 Adsorption Kinetics	gmol//$kg_{sorbent}$/min	0.05-0.07	0.08-0.1
Desorption			
Pressure	bar	0.2-0.3	0.2-0.3
Temperature	°C	<100	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.1	<0.1
Heat of Desorption	kJ/mol CO_2	70	70
CO_2 Desorption Kinetics	gmol/$kg_{sorbent}$/min	N/A	N/A
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	cyclic fixed bed	
Air Flowrate**	kg/hr	1000 - 2800	
Space Velocity	hr^{-1}	7200 - 18000	
Volumetric Productivity	$gmol_{CO2}$/(hr $l_{absorber\ bed}$)	0.1 - 0.3	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>70%	>95% (adaptable depending on use) 1 (adaptable depending on use)
Adsorber Pressure Drop	bar	0.007-0.01	0.005-0.007
Degradation	% capacity fade/cycle	long-term target is 20% in 2-3 years	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A (no absorber/stripper)	

*"Current" taken to mean "today in this project" at 40% completion, and is therefore already a significant improvement on the status quo.

**Module flowrate here refer to a single module in the test plant to be built as part of this project.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

Pressure	**Temperature**	**Composition**						
		vol%					ppmv	
		CO_2	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_X**	**NO_X**
ambient	ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Amine-based sorbent which binds CO_2 by chemisorption

Sorbent Contaminant Resistance – The sorbent is highly resistant to expected contaminants found in the air. Sulfur oxide (SO_X) and nitrogen oxide (NO_X) at levels present in most air are not a key driver of degradation.

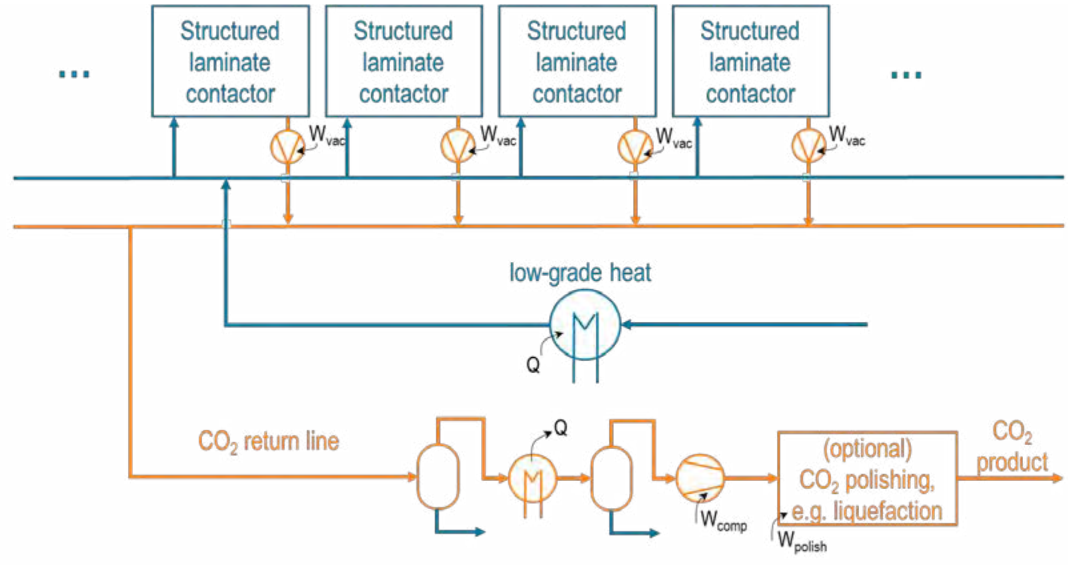
Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent's basic stability to DAC process had been demonstrated prior to this project; the stability of the sorbent and laminate combination over more than 1,000 cycles is a research focus of this project.

Air Pretreatment Requirements – None.

Sorbent Make-Up Requirements – Unknown as of now; the stability of the sorbent + laminate combination over several thousand cycles is one research focus of this project, and this will inform the make-up requirements. The target is to replace the sorbent every two to three years.

Waste Streams Generated – Air depleted in CO_2 is emitted from the contactors. Water is treated and reused in the plant (at full-scale).

Process Design Concept – A block-flow diagram for a full-size plant concept is shown below.



Proposed Module Design – The full-scale plant design will integrate Climeworks' modular DAC "collectors" with Svante's modular structured adsorbent beds. This is a fixed-bed, structured sorbent (laminates) approach. The flowrates in Table 1 above are for individual modules for the test plant being built in California for this project.

TABLE 2: INDUSTRIAL PLANT CARBON CAPTURE / DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Estimate 2035*	Target long-term
Cost of Carbon Removed	\$/tonne CO_2	150-210	~100
Cost of Net Negative Emissions Achieved**	\$/tonne CO_2	170-230	~110
Capital Expenditures	% of total	30-50%	
Operating Expenditures	% of total	50-70%	

* At 1 Mt_{CO_2}/y single plant scale, with a learning rate consistent with total installed volume of 100 Mt_{CO_2}/y assumed.

** Including a full cradle-to-grave life cycle assessment (LCA).

Definitions:

Cost of Carbon Removed – Projected cost of capture and storage per mass of CO_2 under expected operating conditions.

Cost of Net Negative Emissions Achieved – Projected cost of capture and storage per mass of CO_2 under expected operating conditions, when accounting for the associated grey emissions.

Capital Expenditures – Projected capital expenditures in percentage of total costs.

Operating Expenditures – Projected operating expenditures in percentage of total costs.

Calculations Basis – Calculations above are done for a 1 Mt_{CO_2}/y single plant basis, using capital cost values derived from Climeworks' current plants, with scaling factors in the range of 0.6–0.95 depending on the equipment type, with forecasted renewable electricity and heat prices, and with a learning rate assumed for future generations of plants equivalent to a total installed volume of 100 Mt_{CO_2}/y.

Scale of Validation of Technology Used in TEA – The Climeworks DAC systems consist of three major subsystems: the core technology (optimized sorbent/process combination), the full-scale modular CO_2 collectors which house the core technology, and the process plant. This project focuses on the improvement of the core technology (optimized sorbent/process combination). "Estimate 2035" costs are based on the "Current R&D" technical information for the core technology, validated at lab scale over 1,000 cycles of operations. The rest of the plant (collector and process plant) will include incremental improvements of Climeworks' current systems, based on and field proven with the Orca plant in Iceland.

Qualifying Information or Assumptions – A conservative 90% removal efficiency (net-negative emissions achieved/CO_2 removed) is assumed, consistent with external life cycle assessments performed of Climeworks' systems.

technology advantages

- Modular design for easy scale-up.
- Sorbent stability well over 1,000 cycles.
- Good performance due to fast CO_2 uptake in structured adsorbent beds.

R&D challenges

- Work on Gen3 sorbents for improved sorbent lifetime.
- New design geometry of SABs for lower pressure drop.
- Complete optimization of sorbent structure and process for DAC.
- Demonstrate and study structured sorbent's lifetime to estimate costs based on measured data.
- Beyond this project: scale-up sorbent structure to standard module size; number-up collector units; scale-up plant.

status

Gen1 sorbent design and testing of more than 1,000 cycles has been completed, demonstrating sorbent stability and reasonable performance at low relative humidity. The Gen2 sorbent, which uses Climeworks' sorbent with Svante's laminate structure, is currently being tested and has met or exceeded performance targets, significantly improving upon Gen1. The technology maturation plan, preliminary risk assessment, and process flow design have been completed. Purchasing and construction is underway for the California testing and demonstration facility. The collected test data will be used to advise techno-economic and life cycle assessments of the DAC technology.

available reports/technical papers/presentations

Deborah Jelen, "Direct Air Capture Using Novel Structured Adsorbents," Project kickoff meeting presentation, Pittsburgh, PA, March 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11073&filename=Direct+Air+Capture+Using+Novel+Structured+Adsorbents.pdf*.

Deborah Jelen, Adelaide Calbry-Muzyka, "Direct Air Capture Using Novel Structured Adsorbents," presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Jelen.pdf*

Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage Partnership (DAC RECO$_2$UP)

primary project goal

Southern States Energy Board (SSEB) is leading efforts together with AirCapture LLC to advance a solid amine sorbent-based technology for direct air capture (DAC) through field testing in a commercially relevant environment. The primary goal of the DAC RECO$_2$UP project is to decrease the cost of DAC through the testing of existing DAC materials in integrated field units that produce a concentrated carbon dioxide (CO_2) stream of at least 95% purity. This project is focused on engineering design of an integrated DAC system utilizing energy recovery and support services at the National Carbon Capture Center (NCCC).

technical goals

- Conduct applied research and development (R&D) to decrease the cost of DAC from atmospheric air and mixtures of air and simulated industrial gases available in a test bay at the NCCC.
- Develop and scale-up an integrated system utilizing energy recovery at the NCCC.
- Increase the integrated system's fidelity by validating and demonstrating operations in a simulated commercial environment by maximizing capital efficiency and energy efficiency.
- Identify and address key technical barriers, within a representative operating environment, in support of DAC technology commercialization.
- Perform a pre-screening TEA and LCA to determine the environmental sustainability (amount of carbon negativity) and economic viability (cost impacts) of the integrated DAC system.

technical content

The technology, previously developed by Global Thermostat, employs a solid-amine CO_2 adsorption-desorption cycle using a honeycomb-type monolithic contactor impregnated with a solid polyethylenimine polymer that forms agglomerations of polymeric amine capture sites within the mesopores of the contactor. A fan draws air or mixtures of air and CO_2-rich gas streams through the contactor in a laminar flow regime wherein CO_2 is adsorbed by the contactor via diffusion into the contactor walls perpendicular to the airflow. The ultra-low pressure drop monoliths maximize the efficiency of air flow, increasing mass transfer of CO_2 for adsorption. Once the sites bind sufficient quantities of CO_2, the monoliths are then exposed to vacuum and steam heat to desorb the CO_2 from the solid sorbent. The latent heat and hydration from the steam liberates the CO_2 from the amine capture sites and acts as a sweep gas pushing the CO_2 out of the contactor towards a condenser, which condenses the steam back into water for recycle, leaving greater than 98.5% CO_2 gas. The CO_2 is collected and the contactor is cooled via thermal recovery and evaporative heat loss and cycled back to adsorption mode, repeating the cycle.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Contactor with Amine-Based Sorbent for DAC

participant:
Southern States Energy Board (SSEB)

project number:
FE0031961

predecessor projects:
N/A

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partners:
AirCapture LLC; Crescent Resource Innovation; Global Thermostat; Southern Company/National Carbon Capture Center; Synapse Development Group

start date:
10.01.2020

The technology employs a desorption mechanism that leverages a combination of vacuum and low-temperature steam, which together provide a rapid and efficient mechanism of CO_2 desorption while reducing the primary deactivation mechanism of amine oxidation at regeneration temperatures. Laboratory testing has demonstrated the technology's highest efficiency of CO_2 adsorption-desorption mass transfer ratio 10:1 with 900:90 second adsorption-desorption for air concentrations of CO_2. Increasing the technology fidelity in a system capable of continuously cycling 10 contactor assemblies, wherein nine positions are in CO_2 capture mode with one position in regeneration mode, with integrated system architecture and robust operations is required to advance the design. Engineering principles of airflow dynamics, movement of contactors through a cyclically sealed regeneration system, and efficient thermal transfer of low-temperature steam are all well understood.

Detailed laboratory-scale research has been conducted with pre-prototypical configurations using integrated unit operations achieving Technology Readiness Level (TRL) 4. Figure 1 shows a laboratory-scale system used to test and validate monolith adsorption performance, desorption performance, and cycle times. Various tests were carried out on air concentrations of CO_2, along with higher feed concentrations of CO_2, both within co-fed air streams and simulated air streams.

Figure 1: GT's laboratory-scale system used to test and validate monolith adsorption performance, desorption performance, and cycle times.

The laboratory system used the following primary process steps and time/control targets: airflow (5–20 minutes); drain (drain water, 5 seconds); pump down (remove air/O_2 from chamber to prevent oxidation and increase pressure, 10 seconds, 0.2 bar); pressurize (increase pressure in chamber, 10 seconds, 0.6–1.5 bar); regen/CO_2 collection (regenerate monolith, collect CO_2, 30–240 s); and cool (reduce pressure, flash off steam, 0.3–0.6 bar). The heat demand of the system was 4.7 British thermal units (Btu)/g-CO_2 with a pressure drop of 150 pa and sorbent working capacity of 0.1 kg-CO_2/kg.

Figure 2: CO_2 compression, storage, and upgrading skid.

This project invoves a three-phased testing campaign being conducted in an integrated system environment at the NCCC. A DAC skid capable of adsorbing/desorbing CO_2 using GT's solid-amine sorbent monolithic contactors and an energy recovery integration skid that uses process control and heat exchangers to produce the required steam for the DAC process are being constructed and installed at the NCCC. AirCapture is also providing an existing third skid capable of compressing, liquifying, and purifying the CO_2 (Figure 2).

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	2,300	2,300
Bulk Density	kg/m^3	500	500
Average Particle Diameter	mm	0.23	0.23
Particle Void Fraction	m^3/m^3	0.78	0.78
Packing Density	m^2/m^3	1,800	1,800
Solid Heat Capacity @ STP	kJ/kg-K	0.81	0.81
Crush Strength	kg_f	4	4
Thermal Conductivity	W/(m-K)	0.4	0.4
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	2.5	2.5
Heat of Adsorption	kJ/mol CO_2	85-95	85-95
CO_2 Adsorption Kinetics	gmol/kg-min	0.043	0.043
Desorption			
Pressure	bar	1.0	1.0
Temperature	°C	80-100	80-100
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.05	<0.05
Heat of Desorption	kJ/mol CO_2	85-95	85-95
CO_2 Desorption Kinetics	gmol/kg-min	0.3	0.3

Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		Honeycomb Monolith	
Air Feed Approach Velocity	m/sec		5	
Space Velocity	hr^{-1}		120	
Volumetric Productivity	$gmol_{CO2}/(hr\ kg_{sorbent})$		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>50	>95	1.0
Adsorber Pressure Drop	bar		0.002	
Degradation	% capacity fade/yr		5%	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	Ambient	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Solid-sorbent system.

Sorbent Contaminant Resistance – Airborne contamination mitigated with filters.

Sorbent Attrition and Thermal/Hydrothermal Stability – Targeted sorbent lifetime: approximately three years.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Replacement as needed, drop-in.

Waste Streams Generated – Mostly water.

Proposed Module Design – 100 tonne/year DAC modular design together with heat integration skid module and scale-matched CO_2 upgrading/liquefaction module.

technology advantages

- Monolithic contactor provides low pressure drop, low thermal mass, high geometric surface area, and compatibility with various construction methods.
- Adsorption cycle capable capturing greater than 6.5L CO_2 in 900 seconds.
- Desorption cycle releases CO_2 via saturated steam in less than 90 seconds.
- Modular system design enables commercial application in a wide variety of applications.
- Integrated system design for production of high-grade CO_2 from DAC increases overall system exergy.

R&D challenges

- Construction and testing of integrated high-fidelity system in an operational test environment.

status

CFD modelling provided insight in system design and architecture and validated preliminary design concepts. Iterative design based on CFD analysis supported design to maximize overall system energy efficiency and performance. Research efforts are continuing to finalize the design of the desorption chamber sealing mechanism, the construction of a prototype sealing chamber test rig with two different sealing mechanisms, the testing of each mechanism, and the selection of the mechanism to be used when building the DAC system in Budget Period 2. Development of the system design and process model to validate the system timing and anticipated electrical and thermal performance is also ongoing. Construction of the DAC and heat integration skids has commenced.

available reports/technical papers/presentations

Matt Atwood, Bran Raskovic, "Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage (CCUS) Partnership (DAC RECO$_2$UP)," Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11080&filename=Direct+Air+Capture+of+Energy+for+Carbon+Capture%2c+Utilization%2c+and+Storage+(CCUS)+Partnership+(DAC+RECO2UP).pdf*.

Patricia Berry, Matt Atwood, "Direct Air Capture of Energy for Carbon Capture, Utilization, and Storage (CCUS) Partnership (DAC RECO$_2$UP)," Budget Period 1 Review Meeting Presentation, Pittsburgh, PA, October 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11078&filename=Direct+Air+Capture+of+Energy+for+Carbon+Capture%2c+Utilization%2c+and+Storage+(CCUS)+Partnership+(DAC+RECO2UP).pptx*.

A Combined Water and CO_2 Direct Air Capture System

primary project goal

IWVC LLC is developing a transformational hybrid direct air capture (HDAC) technology that simultaneously captures carbon dioxide (CO_2) and water from the air using an amine-functionalized solid sorbent developed by Pacific Northwest National Laboratory (PNNL). In HDAC, a combination of high-performance desiccant and CO_2-selective sorbents are used to remove both the water vapor and CO_2 from the air in a single pass through the HDAC system.

technical goals

- Conduct a detailed design for a 3,000-cubic-feet-per-minute (CFM) HDAC unit to validate the initial electrical, heat, mass, and fluid flow requirements for system.
- Procurement and fabricate the complete HDAC unit.
- Execute the field-testing of the HDAC unit and prepare a final report on the testing, results, conclusions, and recommendations.

technical content

Producing commercially significant amounts of CO_2 from a DAC system requires movement of a large volume of air through the device. Because the emerging field of atmospheric water extraction (AWE) similarly requires movement of large volumes of air, integration of these two technologies into a single overall process has the potential to become more economically and environmentally attractive than if pursued separately. Figure 1 provides an overall schematic of the HDAC system design. The operating principles are simple. The AWE section of the unit utilizes a novel isothermal pressure swing regeneration cycle. First, humid air flows over a desiccant bed that removes moisture. A parallel desiccant bed is isolated from the air stream and simultaneously regenerated under a partial vacuum. The desiccant beds are thermally coupled with heat pipes. Heat pipes provide a highly efficient and passive heat transfer mechanism to “cancel” the heat of water vapor adsorption generated in the active desiccant bed with the endothermic heat of desorption consumed in the desiccant bed undergoing regeneration. Air exiting the desiccant bed thus remains near ambient temperature. The air stream then flows over and helps cool a water vapor condenser, supplemented by process cooling water, so it operates with a minimal ΔT above ambient temperature. The vacuum pump provides suction on the desiccant bed during its regeneration cycle and is used to provide modest compression to raise the vapor pressure sufficiently to condense water. Because the compression work is only done on the water vapor, this minimizes the energy consumption. Lastly, the condensate is pumped up to atmospheric pressure for discharge (consuming trivial additional energy).

The low relative humidity (RH) air stream then enters the second set of sorbent beds that are selective for CO_2 removal and are designed to remove greater than or equal to 85% of the CO_2 from the air stream. Heat recovered from the CO_2 compressor is supplemented with an external low-grade heat source (waste heat, solar, or resistance heating) to thermally regenerate the CO_2 sorbents. The warm/dry air stream is then exhausted to ambient. Using this design approach, the system can capture CO_2 with a zero- or low-carbon footprint.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Combined Desiccant and CO_2 -Selective Sorbent in DAC System

participant:
IWVC LLC

project number:
FE0031970

predecessor projects:
N/A

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start date:
10.01.2020

percent complete:
42%

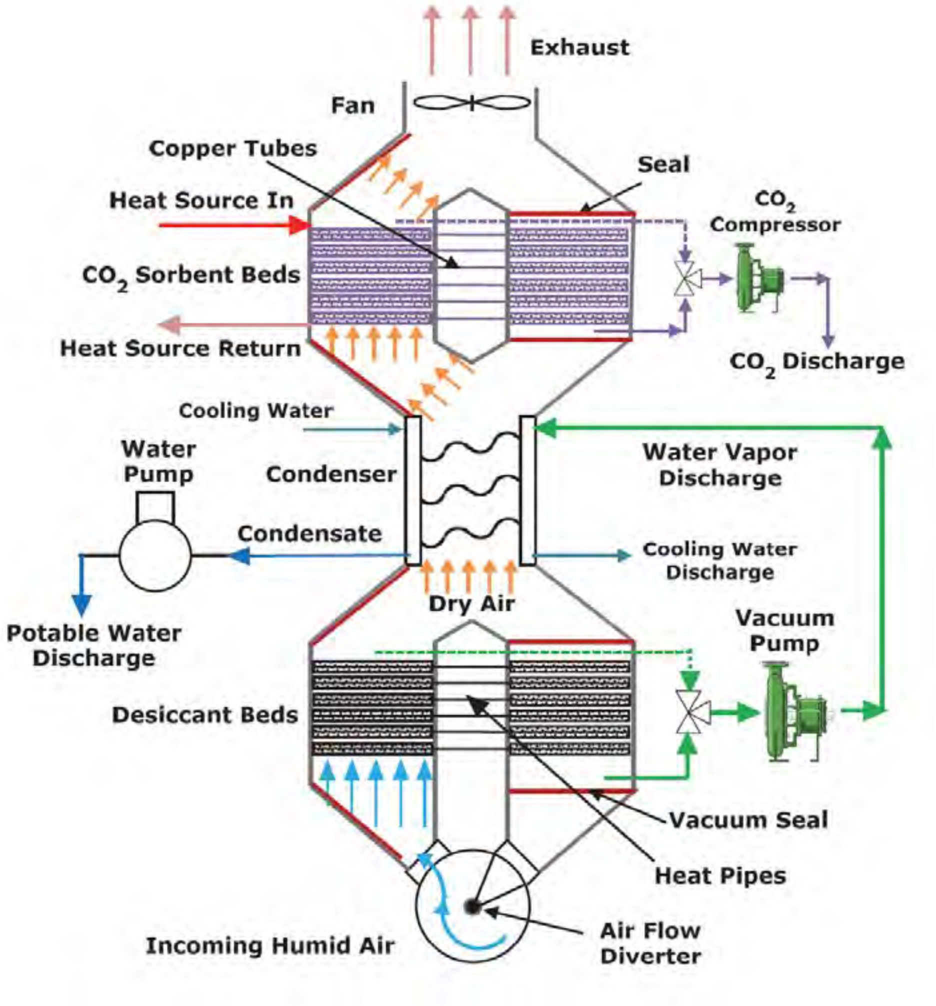

Figure 1: Schematic of HDAC concept.

The project tasks include conducting a detailed design of the HDAC demonstration unit sufficient to provide specifications to individual component manufacturers and parts suppliers for the HDAC unit build; Optimizing the CO_2 sorbent bed cycling to attain at least 95% pure CO_2 discharge stream; evaluating energy savings potential for incorporation of a second sorbent in the DAC section of the design. The idea with the evaluation of a second sorbent is that CO_2 would be released from a physisorbent at lower temperature than the self-assembled monolayers on mesoporous supports (SAMMS) sorbent, thus providing CO_2 mass flow earlier in the regeneration cycle. This bed can also be heated downstream from the SAMMS bed and not reach the same regeneration temperature, thus reducing thermal energy input required to achieve the same CO_2 production rate. The energy savings potential for this second sorbent is being quantified using data on University of South Florida's (USF's) SIFSIX CO_2 sorbent and a recommendation will be provided on whether to include this option in the HDAC demonstration unit.

The SAMMS sorbent for the DAC section is prepared using well-established methods from previous Technology Readiness Level (TRL) 6 efforts at PNNL developing military CO_2 scrubbers. If a decision is made to incorporate the second physisorbent in the final design, the sorbent will be produced at USF and shipped to PNNL for integration into the system. The MOF-303 desiccant will be purchased if available. If not, it can be produced either through a known batch synthesis route or through PNNL's atomization-condensation reactor technology. This technology offers a low-cost and scalable route to produce sorbent materials (e.g., metal-organic frameworks [MOFs]) in bulk quantities. If unexpected cost or production problems develop with MOF-303, there are numerous alternative desiccants with suitable properties that can be substituted.

The sorbent surface coating (both desiccant and DAC) on the aluminum fins is an important step in achieving the uniform sorbent thin film for high diffusive flux of water as well as CO_2 molecules. The plan is to use a cold spray solid-phase deposition process for this step. The cold spray process propels particles in a carrier gas at high velocities. Upon impact with the substrate, a portion of each particle experiences plastic deformation, resulting in mechanical interlocking and metallurgical bonding. A single cold spray nozzle can deposit titanium at rates exceeding 12.5 grams/second and creates coatings as thin as 10 µm. A modified cold spray process is being developed for sorbent deposition/surface coating on the aluminum fins. Cold spray parameters and equipment are optimized such that metallurgical bonding occurs between metal structure and sorbent particles. Typically, cold spray is done with particle diameters of approximately 20 µm. PNNL is installing a powder feeder for fine particles (smaller than 5 µm) to enable direct cold spray of the sorbent powders. Optimal particle velocity and carrier medium (gas or liquid) spray parameters will be identified that produce strong particle-particle bonds while maintaining interconnected porosity for CO_2 and water mass transport into the coating. If necessary, an amine-based polymer can be dissolved in a solvent carrier to enhance binding and adhesion to the aluminum surface and between particles.

The aluminum fin supports with sorbents bonded are assembled into desiccant beds by incorporating the heat pipes/heat supply tubes with the fin supports. Final assembly will include end caps and structural supports for mounting the desiccant beds in their respective housings. The complete assemblies will be shipped to Barr Engineering for incorporation in the HDAC demonstration unit.

technology advantages

- Passive heat transfer mechanism balances the heat of water vapor adsorption generated in the active desiccant bed with the endothermic heat of desorption consumed in the desiccant bed undergoing regeneration.
- System engineering eliminates large thermodynamic inefficiencies with thermal swing regeneration cycles performed in typical AWE designs.
- Combining potable water generation and CO_2 capture in a single device with the unique energy conserving features of the design enables a competitive cost of capture to be achieved with much smaller plant capacities and capital costs than required by conventional DAC systems.
- The integrated DAC and AWE system makes DAC technology deployable in more locations with limited water resources.
- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.

R&D challenges

- Fabrication of HDAC unit.
- Installation and operation of the HDAC unit at the host site.

status

IWVC LLC completed the HDAC detailed design. The San Diego State University—Brawley Test Site limitations were identified and auxiliary equipment was specified (a chiller specified to deal with limited site water so water can be recirculated and an electrical heater specified due to there being no thermal storage onsite). Current efforts involve procurement and fabrication of the HDAC unit.

available reports/technical papers/presentations

Will Kain, "A Combined Water and CO_2 Direct Air Capture System," Direct Air Capture Kickoff Meeting Presentation , Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11101&filename=A+Combined+Water+and+CO2+Direct+Air+Capture+System.pdf*.

Will Kain, "A Combined Water and CO_2 Direct Air Capture System," Project Kickoff Meeting Presentation , Pittsburgh, PA, May 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11102&filename=A+Combined+Water+and+CO2+Direct+Air+Capture+System.pdf*.

Will Kain, "A Combined Water and CO_2 Direct Air Capture System," Budget Period 1 review meeting presentation, Pittsburgh, PA, September 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12465&filename=A+Combined+Water+and+CO2+Direct+Air+Capture+System.pdf*.

Bench-Scale Testing of Monolithic Poly(Propyleneimine) Structured Contactors for Direct Air Capture of Carbon Dioxide

primary project goal

CORMETECH Inc., in partnership with Global Thermostat LLC and Georgia Institute of Technology, is developing and testing a novel sorbent-air contactor composition with low pressure drop optimized for carbon dioxide (CO_2) removal from ambient air. The project is focused on optimizing a monolith contactor to support a next-generation sorbent composition, linear poly(propyleneimine) (l-PPI), which offers advantages over benchmark poly(ethyleneimine) (PEI)-based sorbents for direct air capture (DAC). The novel approach will maximize the volumetric productivity of the DAC process while reducing the auxiliary power required to capture CO_2 from air.

technical goals

- Perform experimental and simulation studies of the novel CO_2 sorbent/gas contactor system based on l-PPI sorbents at DAC-relevant conditions.
- Measure isotherm, kinetic, and transport behaviors of the powder and slab materials.
- Develop a single channel monolith model to optimize the geometry and the meso/macro-porosity of monoliths specifically tuned for l-PPI.
- Develop a transport model based on l-PPI supported on monolith slabs.
- Build and evaluate a single brick sorption tester (SBST) for the bench-scale evaluation of extruded monoliths loaded with l-PPI, enabling the CO_2 sorption performance to be optimized.
- Measure the resistance of the sorbent/contactor composition to oxidation under relevant dry and humid conditions.
- Perform a techno-economic analysis (TEA) utilizing the process model incorporating the novel sorbent/contactor combination.

technical content

Global Thermostat's baseline DAC process employs monolithic, low pressure drop contactors loaded with organic amine molecules or macromolecules to allow for high throughput gas/solid contacting with high volumetric CO_2 sorption productivity. The Global Thermostat DAC process employs relatively shallow honeycomb monolith contactors (~15 cm deep) that permit low pressure drops (hundreds of Pa) at gas approach velocities of 3–5 m s^{-1} while still maintaining a high geometric surface area per unit volume (Figure 1).

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Contactor Impregnated with Novel Sorbent for DAC

participant:
CORMETECH Inc.

project number:
FE0032094

predecessor projects:
N/A

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partners:
Georgia Institute of Technology; Global Thermostat LLC

start date:
09.15.2021

percent complete:
15%

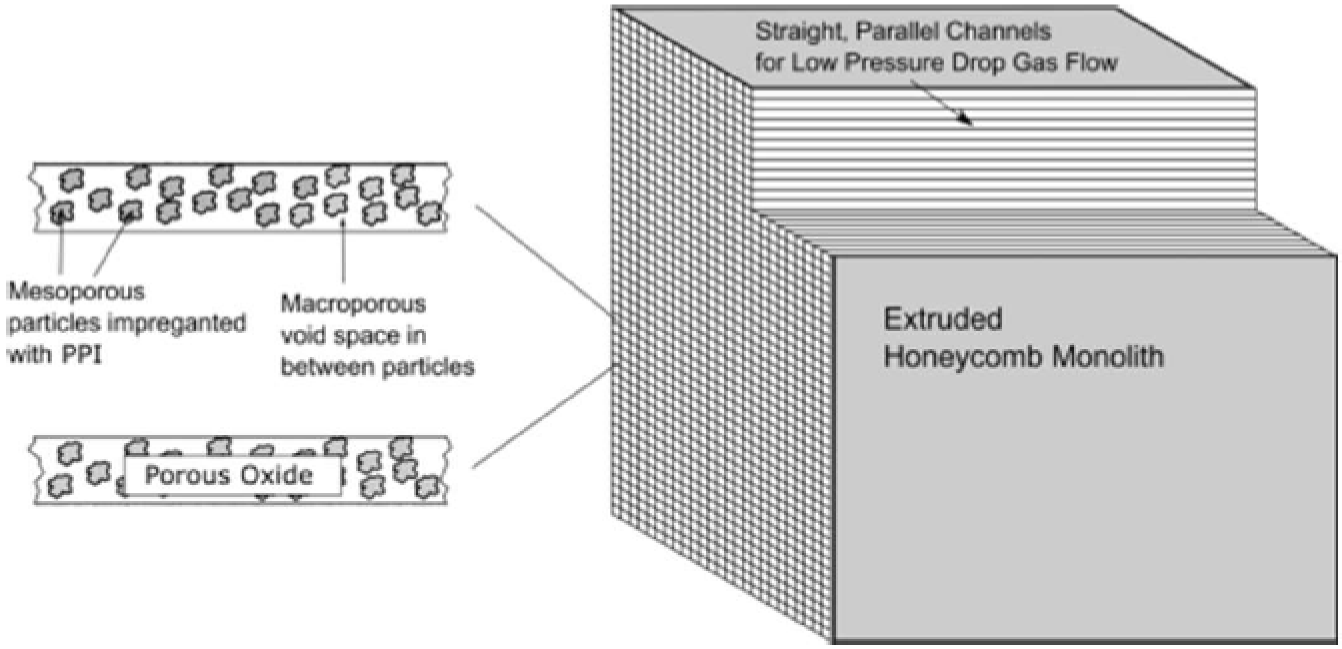

Figure 1: Monolith system used in Global Thermostat process.

After CO_2 adsorption, CO_2 is desorbed and collected by combined temperature-vacuum swing desorption employing steam-stripping, producing a concentrated CO_2 product (Figure 2). Early generations of Global Thermostat's technology used commercially available components that were initially designed and optimized for other applications (e.g., [i] nonporous monolithic contactors with porous oxide washcoats designed for high-temperature catalytic applications and [ii] known commercially available amine compositions). Whereas commercially available materials were leveraged in early development, this project is focused on design and optimization of a gas/solid contactor specifically formulated for DAC.

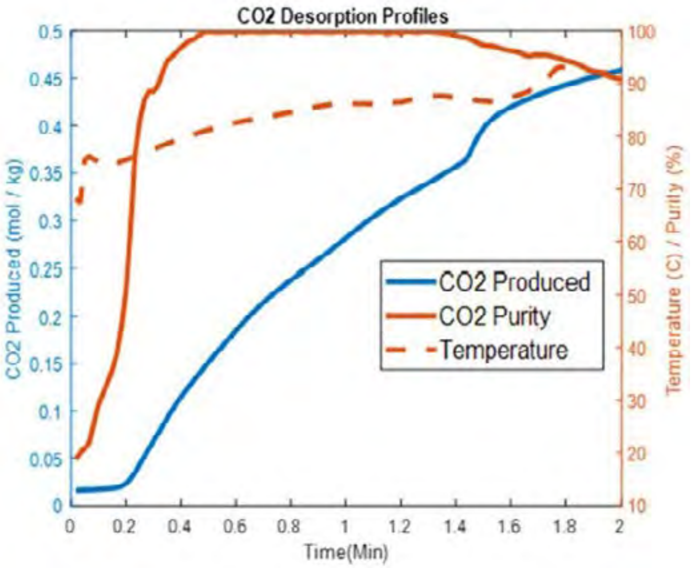

Figure 2: CO_2 desorption using steam regeneration.

Recently, Global Thermostat has developed several generations of amine sorbents with improved properties for DAC in collaboration with Georgia Tech, relative to a baseline commercial amine composition, PEI. Global Thermostat also has collaborated closely with CORMETECH to design and formulate new porous monolith contactors specifically engineered to support PEI amine compositions for DAC. The purpose of this current project is to advance the design of a new monolithic air/solid contactor by developing designs optimized specifically for DAC by tailoring the properties of the monolith contactor to fit synergistically with the next-generation amine composition, l-PPI. The benchmark amine polymer, PEI, is deployed as a branched oligomer. In contrast, the selected next-generation polymer is linear in structure (l-PPI). Given the different structure of the macromolecule (PEI: branched with ethyl linkers, versus l-PPI: linear with propyl linkers), the new polymer can be expected to interface with the porous monolith support differently from the baseline PEI case. In powder tests (data are shown in Figure 3), l-PPI has similar CO_2 sorption properties as PEI, yet superior oxidative stability and water sorption properties (more hydrophobic), making it a promising next-generation amine polymer for DAC. Furthermore, l-PPI has recently been scaled up to the 100-gram quantity levels by project partner Celares GmbH, who is providing sufficient quantities of the polymer needed for monolith-scale testing. Given the promise of l-PPI as a sorbent composition, the focus of this project is to customize a monolith formulation for this next generation sorbent. The project is directed at conducting experimental measurements and formulating a sorption/diffusion/transport model of the adsorption process, which can be used to advance process models and inform process TEAs.

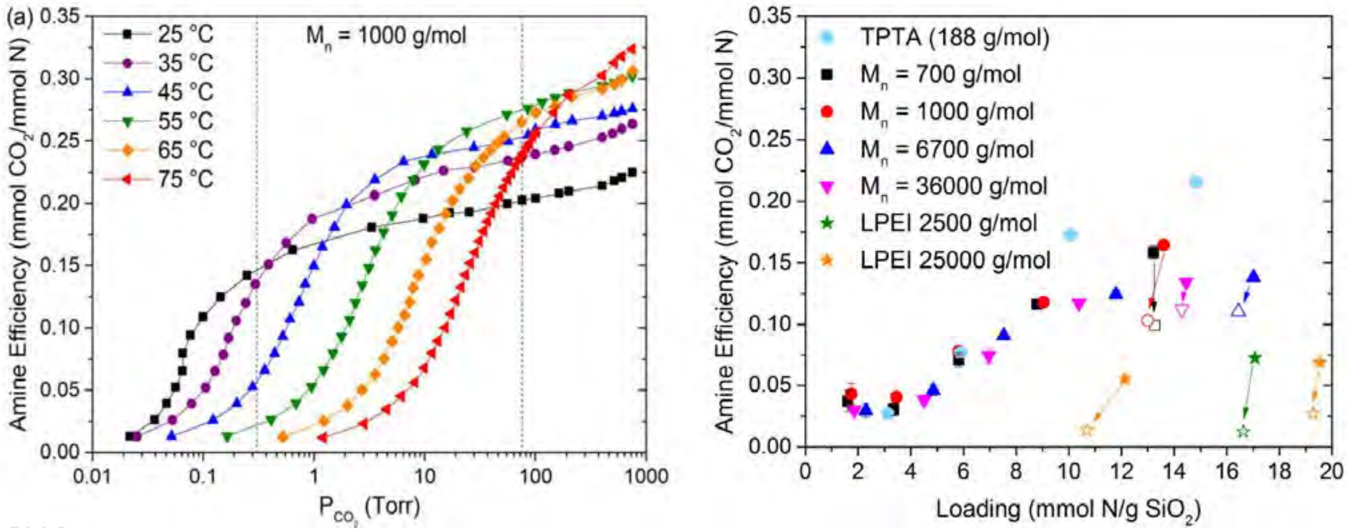

Figure 3. Left: Isotherms at varied temperatures for PPI/SBA-15 sorbents. Right: Amine efficiency versus amine loading for l-PPI versus PEI (closed shapes), 400 ppm CO_2 at 35°C, showing loss after treatment in oxidative environment (open shapes), 21%O_2/N_2, 110° C for 24 hours.

technology advantages

- Monolithic contactor achieves low pressure drop CO_2 capture capability.
- New sorbent with enhanced oxidative stability will improve the on-steam sorbent lifetime in the base Global Thermostat DAC process.
- Utilizes cost-effective fabrication technique from CORMETECH for CO_2 contactor development using porous monolith substrate that can be impregnated with the amine.

R&D challenges

- Synthesis of l-PPI sorbent at kg-scale for full-size optimized monolith brick impregnation and SBST validation testing.
- Development of single-channel monolith with combined momentum, mass, and heat transfer, incorporating porous wall flow and the multi-phase regimes that arise from the use of steam as a desorbing medium, to optimize the monolithic substrate's textural properties for l-PPI and maximize DAC performance.
- Measurement of fundamental transport properties of CO_2 through amine-loaded porous materials and adsorption/desorption equilibria, for model development and incorporation into the single channel monolith model.
- Confirmation of the enhanced oxidative stability of the scaled-up l-PPI sorbent.

status

The project team is currently designing, building, and commissioning the bench-scale SBST unit, along with manufacturing, validation, and bench-scale testing of l-PPI (at kg-scale) using a standard monolithic substrate and the SBST. Development of a single channel model to optimize the geometry and the meso/macro-porosity of monoliths specifically tuned for l-PPI is being conducted. Ongoing efforts include measurement of the adsorption isotherms, kinetic, and transport behaviors of l-PPI, supported on powder and on slab materials to develop an adsorption model and a transport model for inclusion in the single channel monolith model. The process model is also being updated to incorporate the novel sorbent/contactor combination to support the TEA for larger-scale applications.

available reports/technical papers/presentations

Christopher Bertole, "Bench-Scale Testing of Monolithic Poly Propyleneimine Structured Contactors for Direct Air Capture of Carbon Dioxide," Project kickoff meeting presentation, Pittsburgh, PA, October 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12444&filename=Bench-Scale+Testing+of+Monolithic+Poly+Propyleneimine+Structured+Contactors+for+Direct+Air+Capture+of+Carbon+Dioxide.pdf*.

Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture

primary project goal

RTI International is partnering with Creare to design, fabricate, and test, at bench scale, a contactor coated with advanced solid sorbents for direct air capture (DAC) of carbon dioxide (CO_2). The project is focused on the operation of a bench-scale CO_2 removal unit inside an environmental chamber that will maintain constant, controlled test conditions for long-duration life testing (e.g., 1,000 cycles) and parametric testing.

technical goals

- Develop a robust sorbent binder composite coating onto contactor structure.
- Identify the best coating thickness while maximizing the diffusivity and kinetics under optimal sorption and desorption conditions.
- Demonstrate high CO_2 capacity and excellent mechanical durability of coating, and assess the flow versus the pressure drop performance.
- Build a unique test system that will enable rapid, automated cycling of DAC contactors under conditions that simulate operation in a wind-driven system.
- Demonstrate performance and durability in parametric tests across a range of simulated environmental conditions (air speed, ambient temperature, relative humidity).
- Demonstrate long-term performance of the contactor using a controlled air stream (known flow rate, composition, temperature, and pressure) to ensure controlled test conditions over 1,000 cycles.
- Conduct a detailed techno-economic analysis (TEA) and life cycle analysis (LCA) using all experimental data collected.

technical content

The system incorporates RTI's high-performance, high-durability amine sorbents in an innovative air contactor design that is optimized for wind-drive operation. Utilization of Creare's hybrid additive manufacturing technology enables the low-cost fabrication of high-performance, compact structures that exhibit efficient heat and mass exchange transfer and that are ideally suited for integration with sorbent materials. The sorbent/contactor design enables high CO_2 sorption, low regeneration temperature, and excellent tolerance for oxygen and water. The unique environmental chamber being built for testing purposes enables rapid, automated temperature-swing sorption cycling of DAC contactors under conditions that simulate operation in a wind-driven system. Testing in the chamber with constant, controlled test conditions allows for long-term cyclic testing and parametric testing. Ducted fans provide specified air flow rates to simulate constant wind speed throughout the test. Two modules operate 180°C out of phase to maintain steady CO_2 concentration during simultaneous adsorption and desorption operation.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Life Cycle Testing of Passive Sorbent/Contactor for DAC

participant:
Research Triangle Institute

project number:
FE0032099

predecessor projects:
N/A

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partners:
Creare

start date:
10.01.2021

percent complete:
25%

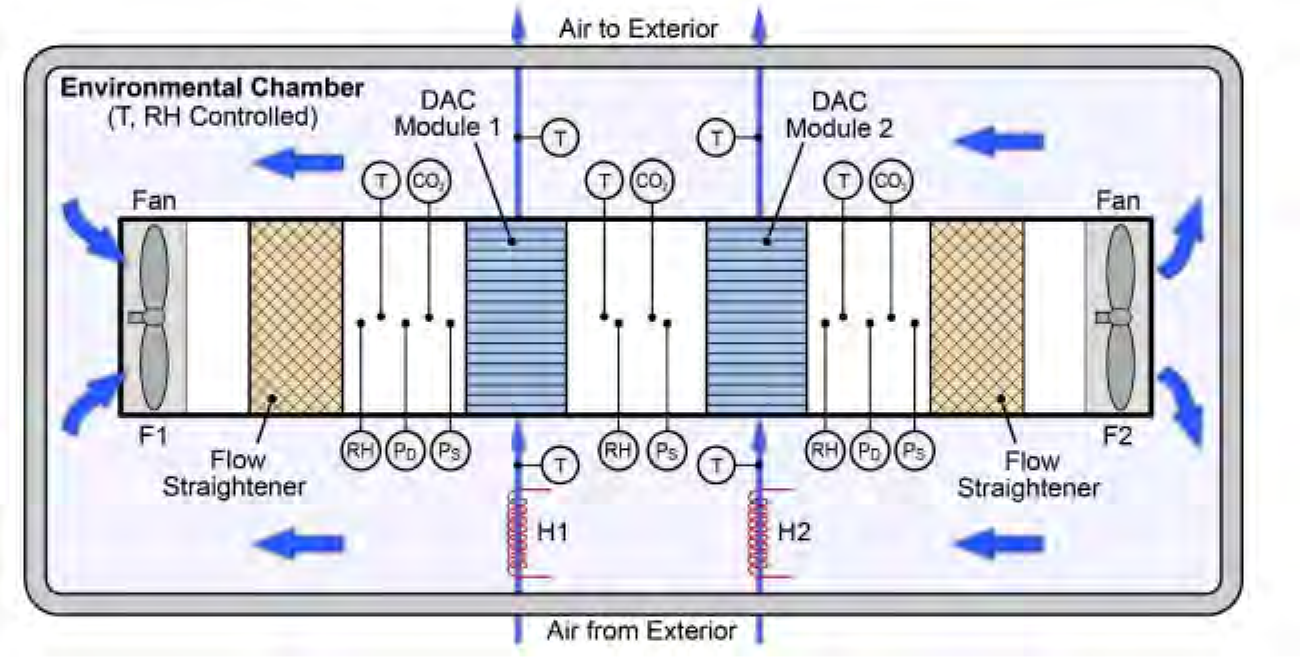

Figure 1: Test chamber for long-term testing of contactor modules.

technology advantages

- Rapid and simple temperature-swing sorption cycling.
- Highly efficient mass transfer and low flow resistance of contactor enables low-power, wind-driven operation.
- Low-cost additive manufacturing process for fabrication of contactor.
- High surface area contactor designed with parallel-plate micro-channels.
- This project leverages the knowledge and experience gained through the Advanced Research Projects Agency–Energy (ARPA-E) efforts to complete the development of a bench-scale DAC process by optimizing the sorbent binder composite coating and enabling long-term cyclic testing to prove performance and durability.

R&D challenges

- Sorbent coating durability and CO_2 sorption and regeneration performance during long-term cycling under relevant DAC conditions.
- Achieving a uniform sorbent coating layer with a thickness ≤ 10 mil (e.g., 0.254 mm) and strong film adhesion to the stainless steel plate surface.
- Achieving efficient CO_2 capture under minimal wind conditions.

status

The project commenced in October 2021. The project team is preparing a sorbent coating formulation. Polymers under consideration as coating binders are phenolic resins, epoxy novolac resins, acrylates, and many others.

available reports/technical papers/presentations

Mustapha Soukri, "Accelerated Life Cycle Testing of Advanced Structured Material Systems for Direct Air Capture," Kickoff Meeting Presentation, December 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12664&filename=Accelerated+Life+Cycle+Testing+of++Advanced+Structured+Material++Systems+for+Direct+Air+Capture.pdf*.

Bench-Scale Development of a Novel Direct Air Capture Technology Using High-Capacity Structured Sorbents

primary project goal

Susteon Inc., in partnership with Cormetech Inc. and Columbia University, is conducting bench-scale testing on a novel structured sorbent system for direct air capture (DAC). The project team is developing a structured material system (SMS) that integrates a highly dispersed sorbent with in situ desorption by direct electric heating and a low pressure drop structured support in order to reduce the overall cost of DAC by lowering energy consumption by approximately 50%.

technical goals

- Advance the novel SMS from the current Technology Readiness Level (TRL) 3 to TRL 4 to justify its scale-up and pilot test in a subsequent program.
- Optimize the sorbent and structured support to maximize CO_2 working capacity, capture/adsorption rate, and adsorbent stability.
- Design and build a bench-scale test unit to evaluate the SMS and determine engineering factors and scale-up parameters such as CO_2 working capacity, adsorption and desorption rates, desorption energy requirements, and cycle times.
- Evaluate desorption method and refine the current COMSOL-based desorption heating method model to design an energy-efficient, facile, and cost-effective means to integrate desorption energy into the SMS.
- Develop and validate a process model using lab- and bench-scale data.
- Perform techno-economic analysis (TEA) and life cycle analysis (LCA) studies to assess the potential of the novel structured sorbent to reduce the cost of DAC by more than 20% compared to current technologies.

technical content

DAC is a potentially scalable negative CO_2 emissions technology. Beyond the benefit of negative emissions, DAC technologies can use CO_2 for a wide variety of applications, ranging from CO_2 conversion to value-added products to geologic storage without expensive pipelines. The U.S. Department of Energy (DOE)—Office of Fossil Energy and Carbon Management (FECM)/National Energy Technology Laboratory (NETL), Office of Energy Efficiency and Renewable Energy (EERE), and Advanced Research Projects Agency-Energy (ARPA-E)—and industry are making significant investments in the development of these technologies. With the exception of those developed by three major providers (Carbon Engineering, Climeworks, and Global Thermostat), most DAC technologies are under bench-scale development. A majority of these are based on solid adsorbents, primarily containing amine (e.g., polyethylene imine [PEI]) as a reactive chemical agent for CO_2, and almost all of them are supported on a high surface area support material, like a silica and/or a metal organic framework (MOF). These materials are scientifically intriguing, but their scale-up to commercial quantities at a reasonable production cost and their limited selectivity

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structured Sorbent System with Direct Electric Heating for Desorption in DAC Process

participant:
Susteon Inc.

project number:
FE0032118

predecessor projects:
N/A

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partners:
Cormetech Inc.;
Columbia University

start date:
10.01.2021

percent complete:
17%

for adsorbing CO_2 over water (H_2O) from air are major challenges standing in the way of commercialization for DAC applications. This project's technology uses alkali sorbents, primarily sodium-based materials on an alumina support. The CO_2 in this process is captured by the synergistic combination of physical adsorption by high surface area alumina support followed by chemisorption by sodium carbonate (Na_2CO_3).

At ambient temperatures, CO_2 chemisorption on Na_2CO_3 is highly favorable, bringing CO_2 concentration in air down from 415 to less than 25 parts per million-volume (ppmv), while at higher temperatures the reverse reaction is favored, decomposing sodium bicarbonate ($NaHCO_3$) into Na_2CO_3 and CO_2.

Susteon has been working with Columbia University for the last two years to develop dual-function materials for reactive CO_2 capture, both from flue gas and for reactive DAC applications (Small Business Innovation Research [SBIR] grant DE-SC0020795). This collaboration has led to the identification of unique sorbent materials that exhibit very desirable characteristics for DAC applications. It was found that moisture in the air significantly enhances the performance and stability of the sorbent, unlike MOF-based sorbents, which selectively adsorb H_2O over CO_2. A high degree of dispersion of Na_2CO_3 on high surface area alumina allows rapid adsorption and desorption rates. Using the sorbent compositions identified, a structured DAC sorbent system capable of capturing CO_2 from air at a rapid rate and high dynamic capacity was developed by washcoating a low pressure-drop monolithic structure while minimizing heat/energy needed to desorb the captured CO_2. In this project, the sorbent is being incorporated on commercially available monolith supports (for low-cost fabrication) to minimize pressure drop.

The major cost contributor to DAC is the high regeneration temperature and energy input requirement for CO_2 desorption. In the case of Susteon's DAC technology, favorable sorbent characteristics enable CO_2 to be desorbed below 120°C with heat generated using renewable electricity. Relying purely upon temperature-swing adsorption, this technology does not require partial pressure difference as a driving force for desorption, as is the case with other amine-based DAC sorbents that use steam to lower the CO_2 partial pressure. This enables energy savings via lowered temperature requirements for sorbent regeneration and a reduction in auxiliary energy requirements such as vacuum and steam generation.

One of the key components of the SMS in Susteon's DAC technology is an electrical heating component that enables selective heating of the sorbent to facilitate CO_2 desorption. Selective heating leads to minimal wasted heat and high energy efficiency, while the overall low temperature requirement for sorbent regeneration enables Susteon's engineered DAC solution to be powered entirely by carbon-free energy (e.g., solar, wind). Other advantages of the SMS relative to other leading DAC sorbents include high sorbent working capacity (~3 wt%) and long-term stability, sorbent resistance to atmospheric oxygen and humid conditions, fast adsorption and desorption rates, and the environmentally benign nature of the sorbent materials.

Figure 1 shows a process flow diagram for a fully engineered DAC technology, which includes both the sorbent-containing SMS and supporting downstream systems. During the adsorption step at ambient conditions, CO_2 is adsorbed onto the sorbent contained within channels in the SMS, with air drawn into the system using a fan. The SMS is then closed to the air, and a fan evacuates CO_2-lean air from the system. Renewable electricity is used to selectively heat the sorbent whereupon the CO_2 is desorbed, regenerating the sorbent. A vacuum pump pulls high-concentration CO_2 (containing some water vapor) from the system. Water is condensed out and the pure CO_2 is compressed and sent for storage.

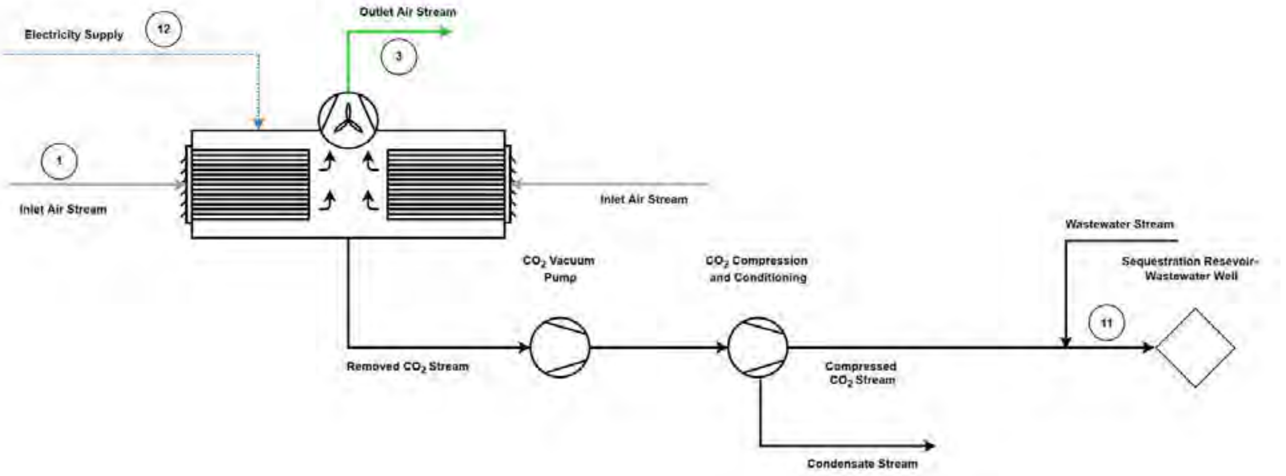

Figure 1: Process flow diagram for the Susteon DAC technology.

Chemical/Physical Sorbent Mechanism – Chemisorption with temperature swing.

Sorbent Contaminant Resistance – High.

Sorbent Attrition and Thermal/Hydrothermal Stability – Proprietary.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Proprietary.

Waste Streams Generated – N/A.

Process Design Concept – Figure 1 (above) illustrates the process design concept for Susteon's DAC technology.

Proposed Module Design – The key components of Susteon's DAC module include: (i) a solid sorbent, consisting of an alkali carbonate as a CO_2 getter; (ii) a monolith to support the sorbent and allow air flow through the module; (iii) a layer of resistive material to selectively heat the sorbent; (iv) an enclosure to house the supported sorbent; (v) mechanical components such as fans and louvers to draw air into the module and enable a product stream of pure CO_2; (vi) necessary gas handling and process control systems. The module operates by temperature-swing adsorption principles.

TABLE 1: KEY TECHNOLOGY METRICS FOR DIRECT AIR CAPTURE

Values	Units	Current R&D Value	Target R&D Value
Carbon Capture Capacity	w/w % sorbent	2.5	3.5
Heating Rate	°C/min	10	75
Energy Intensity	kWh/tonne CO_2	3,335	<2,500
Capital Expenditure Intensity	$/tonne CO_2	1,050	<800

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – Susteon has performed a preliminary engineering and TEA on its DAC technology at multiple scales, including the present lab scale (~1 kg/day CO_2 removal), 100 tonnes/day CO_2 removal, and 1,000,000 tonnes/year CO_2 removal. Based on this TEA, Susteon believes that there is a reasonable pathway to achieve $100 per tonne of CO_2 capture cost at 1 million tonnes/yr scale assuming electricity price of ~3 cents/kWh and capital intensity of ~$600/tonne-year.

Scale of Validation of Technology Used in TEA – Susteon has validated the key innovations of the proposed DAC technology at the laboratory scale, corresponding roughly to TRL 3.

technology advantages

- Novel electrical heating subsystem to minimize heat losses, lowering regeneration energy penalty.
- Low cost of sorbent and higher CO_2 capture rate and capacity compared to amine-based sorbents.
- Sodium carbonate sorbent has favorable impact of moisture compared to MOF sorbents, and easy regenerability at less than 120°C.

R&D challenges

- Implementation of integrated electrical heating technology in the structured support material.

status

Susteon Inc. has begun sorbent development, optimization, and characterization work. The work focuses upon high surface area sorbent dispersed on the selected support structure to achieve maximum capacity, sorption rate, and adsorbent stability.

available reports/technical papers/presentations

N/A.

Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 Using an Additively Manufactured Contactor

primary project goal

General Electric Research (GE) is collaborating with the University of California at Berkeley (UCB) and the University of South Alabama (USA) to develop an advanced integrated reticular sorbent-coated system to capture carbon dioxide (CO_2) using an additively manufactured contactor (AIR2CO2 Contactor). The project team's key objective is to develop and test a bench-scale (1 kg CO_2/day) direct air capture (DAC) system that consists of two low-pressure drop AIR2CO2 Contactors that alternate adsorption/desorption cycles for continuous CO_2 removal from ambient air.

technical goals

- Scale-up synthesis of the optimized MOF-808-Lys for sorbent integration and refinement of the sorbent cost model (UCB).
- Perform systems engineering and computational fluid dynamics (CFD) modeling for bench-scale AIR2CO2 Contactor system (GE and USA).
- Construct and test contactor components for pressure drop and adapt sorbent-binder composite coatings developed under FE0031956 onto these components to evaluate CO_2 capture performance under DAC conditions (GE and USA).
- Fabricate a bench-scale (up to 1 kg CO_2/day) AIR2CO2 Contactor system and evaluate performance.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA) of the AIR2CO2 Contactor system.

technical content

The AIR2CO2 Contactor program combines UCB's metal-organic framework (MOF) sorbents (Figure 1) for CO_2 capture and GE's sorbent-binder composite formulation and coating process in an additively manufactured, low pressure drop contactor (Figure 2). Operation of the integrated system will allow for continuous removal of CO_2 from air via alternating temperature vacuum swing adsorption/desorption cycles. The coated component performance characteristics and process conditions are summarized in Table 1, along with target performance metrics for an optimized sorbent-coated contactor.

A major focus of the program is to evaluate various prototype contactor (e.g., hydraulic diameter) and sorbent coating (e.g., coating thickness) properties as a function of gas flow rate to understand the effects on pressure drop across the contactor. CFD modelling is performed to reach an understanding of the CO_2/H_2O transport process at relevant length scales (micropore and macropore scales) and

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Novel Additively Manufactured Air Contactor with Integrated Sorbent

participant:
General Electric Research

project number:
FE0032126

predecessor projects:
FE0031956

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partners:
University of California Berkeley; University of South Alabama

start date:
10.01.2021

percent complete:
15%

complimented by experiments to understand the impact of the coating on sorbate diffusion resistances.

The project tasks are to: 1) produce a bench-scale contactor by scaling the contactor fabrication and sorbent-coating processes; 2) validate the CFD model and pressure drop predictions; 3) fabricate a second bench-scale contactor and combine with the relevant balance of plant components (e.g., fans, steam generator, vacuum pump, etc.); 4) evaluate the contactor system against the performance criteria detailed in Table 1 under DAC conditions; perform iterate experimentation with varying process conditions to understand the operating envelope of the AIR2CO2 Contactor system for removal of up to 1 kg CO_2/day from ambient air; and 5) utilize outputs of the sorbent scaling efforts, the CFD modelling, and CO_2 capture experiments to develop a TEA and LCA of the full AIR2CO2 Contactor system.

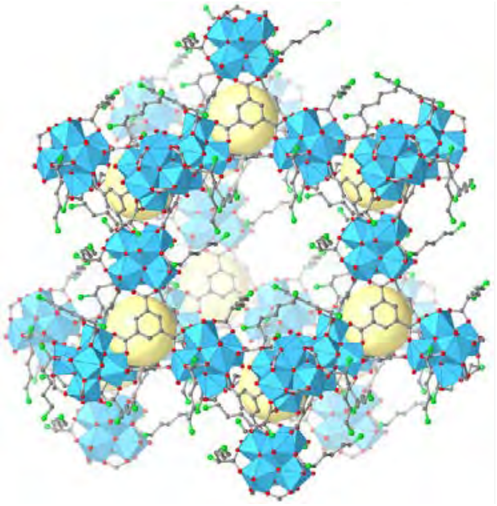

Figure 1: MOF-808-Lys sorbent.

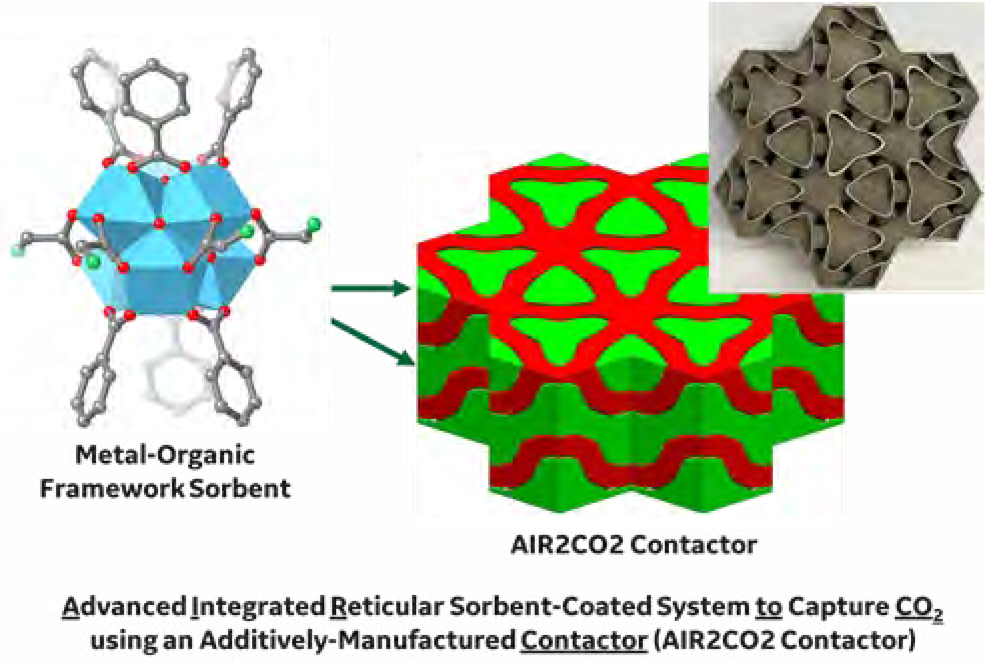

Figure 2: AIR2CO2 Contactor project (FE0032126). Sorbent-coated contactor design showing sorbent-integrated channels (green) and hot air channels for desorption (red).

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	520	520
Bulk Density	kg/m^3	350	350
Average Particle Diameter	mm	0.002-0.01	0.002-0.01
Particle Void Fraction	m^3/m^3	0.3	0.3
Packing Density	m^2/m^3	~2.7 x 10^5	~5.6 x 10^5
Solid Heat Capacity @ STP	kJ/kg-K	0.866	—
Crush Strength	kg$_f$	Not applicable	Not applicable
Attrition Index	-	Not applicable	Not applicable
Thermal Conductivity	W/(m-K)	0.125	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.07	2.3
Heat of Adsorption	kJ/mol CO_2	72	72
CO_2 Adsorption Kinetics	gmol/kg·min	5.5 x 10^{-4}	0.2
Desorption			
Pressure	Bar	<0.0004	<0.0004
Temperature	°C	100-120	80-110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.01	0.25
Heat of Desorption	kJ/mol CO_2	72	72
CO_2 Desorption Kinetics	gmol/kg·min	1.1 x 10^{-4}	0.2
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr^{-1}	150,000	
Volumetric Productivity	gmol$_{CO2}$/(hr l$_{absorber\ bed}$)	2	
CO_2 Recovery, Purity, and Pressure	% / % / bar	70 95 —	
Adsorber Pressure Drop	Pa	150	
Degradation	% capacity fade/cycle	0.0001	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed-Gas Assumptions –

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7 psia	-70 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Fundamental process by which the sorbent materials adsorb or react with gases of interest. At high CO_2 partial pressures, both chemisorption and physisorption of CO_2 occurs. At DAC conditions (0.04 kPa CO_2), only chemisorption of CO_2 occurs.

Sorbent Contaminant Resistance – Ability for the solid sorbent materials to perform under direct air conditions despite the presence of volatile components coming in contact with the sorbent-integrated contactor system. Nitrogen oxide (NO_X) is not expected to have a significant impact on sorbent performance; however, reaction of amine-based sorbents with sulfur oxide (SO_X) to form heat-stable salts is a known issue that will slowly decrease sorbent capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Evaluation of the performance and life of the solid sorbent materials as a result of exposure to temperature and relative humidity. Long-term thermal/hydrothermal stability of the sorbent-binder composite under operating conditions is being investigated.

Waste Streams Generated – Waste gases that are produced as a result of CO_2 capture and release.

technology advantages

- A compact, low pressure drop, sorbent agnostic contactor design that can only be fabricated using additive manufacturing
- Lower energy potential compared to conventional solvents.
- Tailored reticular sorbent-binder structured material composite with the potential for high capacities, rapid sorption kinetics, and robust cycle performance.
- Modular and scalable contactor system that enables alternating capture and release of atmospheric CO_2.

R&D challenges

- Ability to achieve 1 kg CO_2/day bench-scale testing of coated additively printed parts.
- Achieving the desired energetics and cost of capture.
- Scale-up potential: demonstration scale with full-size additive contactor.
- Understanding the mass transfer mechanisms of the integrated sorbent/contactor system.
- Lack of sorbent coating uniformity and hysteresis result in rapid system degradation.
- Insufficient sorbent-binder composite capacity and slow CO_2 capture/release kinetics.

status

Project has begun. CFD modeling and sorbent characterization are underway concurrently. Contactor geometry modelling is complete and pressure drop testing of various contactor components is underway.

available reports/technical papers/presentations

Moore, D., "AIR2CO2 Contactor Kick-Off: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 Using an Additively-Manufactured Contactor." NETL/DOE Kickoff Meeting Presentation. December 6, 2021. *https://netl.doe.gov/projects/plp-download.aspx?id=12536&filename=Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+Carbon+Dioxide+(CO2)+Using+an+Additively-Manufactured+Contactor+(AIR2CO2+Contactor).pdf*.

Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation

primary project goal

The University of Cincinnati (UC) is developing a revolutionary carbon dioxide (CO_2) capture system optimized for direct air capture (DAC). The technology utilizes an adsorption-regeneration cycle with a proprietary aminopolymer-silica hybrid adsorbent. UC is being assisted by BASF Catalysts and Daeyoung C&E in developing the sorbent-washcoated monolith structure and Trimeric for the economic analysis.

technical goals

- Perform a computational fluid dynamics (CFD) analysis to model fluid mechanics and adsorption kinetics to establish baseline adsorbent geometry.
- Manufacture sorbent in-house. Establish long-term lab-scale performance criteria.
- Manufacture sorbent-washcoated monolith structure.
- Design, construct, and test air contactor structure.
- Design, construct, and test full DAC system.
- Evaluate performance of adsorbent-washcoated monolith in air contactor/DAC system.
- Perform a techno-economic analysis (TEA) and life cycle analysis (LCA) and construct a state-point data table for the whole system.

technical content

UC is developing a new adsorbent material with a proprietary hybrid blend of aminopolymer and silica with a washcoated monolith structure. The new adsorbent is slated to be used in a DAC system that constructed in partnership with BASF Catalysts and Daeyoung C&E. Trimeric is assisting in carrying out a full-scale TEA and LCA for the complete DAC system. The scope of work for this project consists of the determination of CO_2 adsorption kinetics (via process modeling through a CFD study); sorbent manufacturing; development of the sorbent-washcoated monolith structure; the design, fabrication, and operation of a passive air contactor; performance evaluations; and TEAs and LCAs. The DAC system design makes use of a novel air contactor system that is slated to maximize CO_2 throughput with minimal external energy requirements (less than 80 kJ/mol CO_2 for desorption). The sorbent is being designed to be resistant to both oxidative and thermal degradation with cost-effective scalability. The air contactor is being designed for high air throughput with minimum pressure drop. The process parameters of the complete DAC sorbent system are shown in Table 1, while a schematic of the air contactor system is shown in Figure 1.

program area:

Carbon Dioxide Removal

ending scale:

Bench Scale

application:

Direct Air Capture

key technology:

Sorbents

project focus:

Sorbent-Washcoated Monolith in Air Contactor System

participant:

University of Cincinnati

project number:

FE0032128

predecessor projects:

N/A

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partners:

BASF Catalysts LLC; Daeyoung C&E Co.; Trimeric

start date:

10.01.2021

percent complete:

20%

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	2,050	2,050
Bulk Density	kg/m^3	810	810
Average Particle Diameter	mm	0.05	0.02-0.05
Particle Void Fraction	m^3/m^3	0.3	0.3-0.4
Packing Density	m^2/m^3	470,000	TBD
Solid Heat Capacity @ STP	kJ/kg-K	1.30	1.30
Crush Strength	kg_f	Not applicable	TBD
Attrition Index	-	~7-10	~7-10
Thermal Conductivity	W/(m-K)	Not available	TBD
Manufacturing Cost for Sorbent	$/kg	4-8	4-8
Adsorption			
Pressure	bar	1.013	1.013
Temperature	°C	0-40	0-40
Equilibrium Loading	g mol CO_2/kg	1.8-2	1.8-2
Heat of Adsorption	kJ/mol CO_2	66	66
CO_2 Adsorption Kinetics	gmol/(kg sorbent×min)	~0.05-0.08	~0.05-0.08
Desorption			
Pressure	bar	0.3-1	0.3-1
Temperature	°C	70-100	70-100
Equilibrium CO_2 Loading	g mol CO_2/kg	~0.1	~0.1
Heat of Desorption	kJ/mol CO_2	~120	~120
CO_2 Desorption Kinetics	gmol/(kg sorbent×min)	~0.4-0.6	~0.4-0.6
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Flow though monolith in air contactor, adsorption-desorption cycles	
Flue Gas Flowrate	kg/hr	~4-16	
Space Velocity	hr^{-1}	5,000-20,000	
Volumetric Productivity	$gmol_{CO2}$/(hr x V(L) $_{absorber\ bed}$)	~2	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90% >95%	1.0325
Adsorber Pressure Drop	bar	0.002	
Degradation	% capacity fade/cycle	0.005	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	Not available	

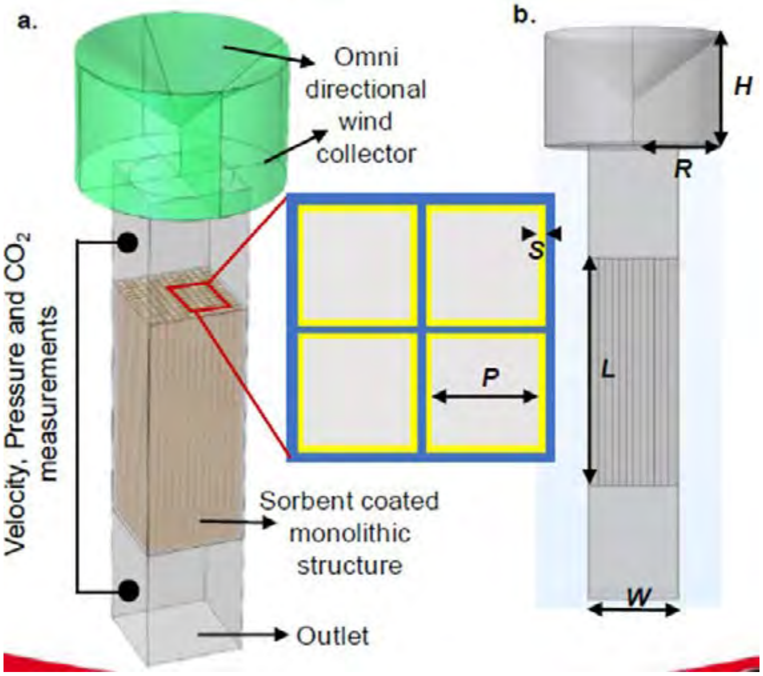

Figure 1: Passive air contactor (a) isometric view and (b) side view.

One of the core strengths of the new adsorbent mixture is the resistance to oxidative and thermal degradation. Figure 2 highlights the performance of the proposed sorbent compared to that of a conventional one of similar chemical makeup. The modified aminopolymer/silica blend suffers significantly less weight loss over time and is able to maintain high performance for more than 30 times longer than the conventional sorbent blend.

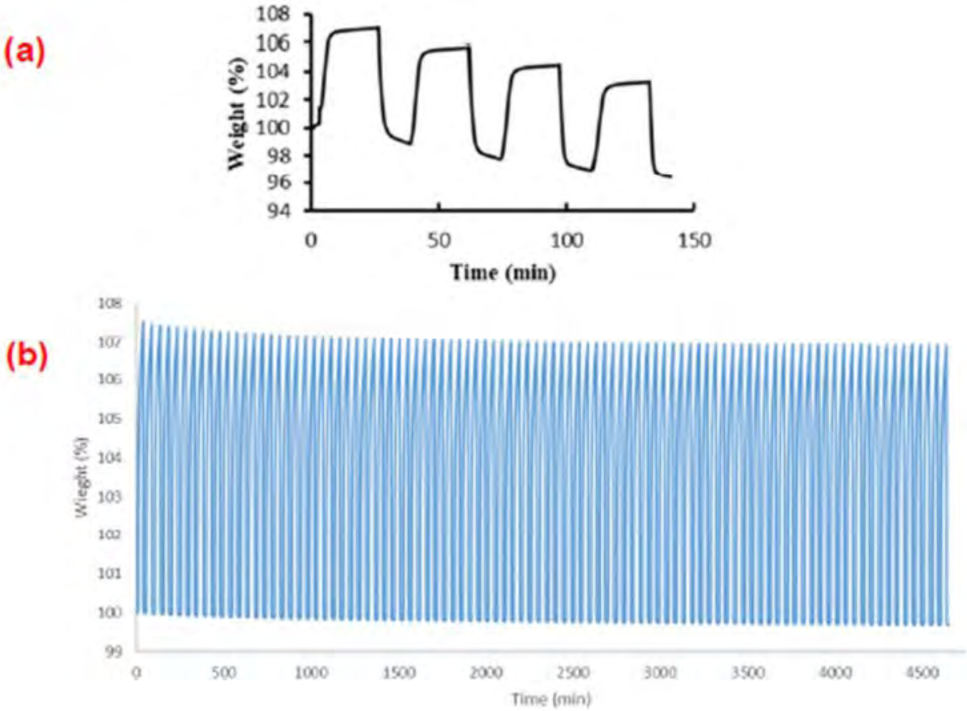

Figure 2: Degradation performance (@ 25°C, 400 ppm CO_2 in dry air) of (a) conventional aminopolymer/silica and (b) modified aminopolymer/silica.

A TEA is being performed as a part of this study. Predicted and target economics results are shown in Table 2.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	150	100
Cost of Carbon Avoided	\$/tonne CO_2	n/a	n/a
Capital Expenditures	\$/tonne CO_2	n/a	n/a
Operating Expenditures	\$/tonne CO_2	n/a	n/a

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Feed Gas Assumptions –

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	50-105 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical adsorption by complex formation.

Sorbent Contaminant Resistance – Selectivity toward CO_2 over H_2O and resistance to O_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition is dependent on sorbent coating onto monolith and the monoliths are being prepared using the proprietary formulations of BASF and Daeyoung C&E. Thermal stability is warranted by controlling temperature and pressure conditions for desorption.

Flue Gas Pretreatment Requirements – N/A.

Sorbent Make-Up Requirements – Sorbent make-up rate is determined from long-term cyclic evaluations of the sorbent.

Waste Streams Generated – Waste gases (mostly water).

technology advantages

- Lower degradation rate: longer lifespan.
- Low required desorption energy input (<80 kJ/mol).
- Air contactor requires no external energy input.
- High CO_2 purity (>95%).
- High CO_2 adsorption selectivity.
- Low air-side pressure drop.

R&D challenges

- Development of the sorbent-washcoated monolith structure.
- Establishing the CO_2 adsorption kinetics.

status

The project has begun. A CFD analysis for the air contactor design is underway and lab-scale evaluation of the CO_2 sorbent is progressing.

available reports/technical papers/presentations

Lee, J., 2022, “Energy-Efficient Direct Air Capture System for High-Purity CO_2 Separation.” Project Kickoff Meeting. DOE/NETL. Pittsburgh, PA. March 7. *https://netl.doe.gov/projects/plp-download.aspx?id=12948&filename=Energy-Efficient+Direct+Air+Capture+System+for+High+Purity+CO2+Separation.pdf*.

Hybridizing Heat-Integrated 3D-Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents

primary project goal

Georgia Tech Research Corporation (GTRC), and project partners Oak Ridge National Laboratory (ORNL), ReactWell LLC, and Trimeric Inc., are advancing a fiber sorbent technology for direct air capture (DAC) through optimization of a contactor design to enhance productivity and lower cost. Polyethyleneimine (PEI)-infused cellulose acetate (CA)/silica fiber sorbents previously developed for DAC applications are being housed in 3D-printed modules that provide heat integration and flow control for adsorption of carbon dioxide (CO_2). The hybridization of fiber sorbent technology with modular housing provides several advantages that lead to lower air pressure drops, higher sorbent productivity, and ease of manufacturing and assembly. Budget Period 1 (BP 1) project tasks are to: 1) fabricate the fibers on a large-scale, with a portion woven into laminate-style sheets; 2) design, fabricate, and optimize the hybrid 3D-printed modules 3) conduct long-term cyclic testing at bench scale on the optimal 3D-printed module. BP 2 tasks are to: 1) evaluate the hybrid modules containing the fibers against pressure drop, productivity, purity, and degradation metrics 2) optimize the hybrid system to yield CO_2 purity of at least 95% with a volumetric productivity five times greater than state-of-the-art.

technical goals

- Fabricate the 3D-printed modules and fiber sorbents (GTRC and ORNL).
- Experimentally evaluate the performance of the assembled hybrid modules and further optimize the design (GTRC).
- Complete modeling and a full techno-economic analysis (TEA) and update the model with experimental results (GTRC and Trimeric).
- Test the hybrid modules in a long-term cycling study (ReactWell).

technical content

The overall objective is to research, develop, and evaluate a modular DAC system that is simple and scalable. This system is based on the adsorption of CO_2 into commercial polyamines supported by porous fiber sorbents, which can be produced at kilometer-per-hour scales using the project's pre-pilot spinning line. The project goal is to increase the already-high productivity of these fiber materials via novel 3D-printed modular housing systems that provide easy-to-manufacture and localized heat integration and flow control (Figure 1). This hybridization of fiber sorbent technology with modular housing provides several advantages that lead to lower air pressure drops and higher sorbent productivity, as well as an ease of manufacturing and assembly that is unrivaled by existing and emerging heat-integrated contactor designs.

The design of the modular housing is one of the key enabling features of this new DAC approach, as the manufacturing of the fiber sorbents is a routine practice in the project's facility. The modular housing is being fabricated with the following

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
3D-Printed Modules Integrated with Fiber Sorbents

participant:
Georgia Tech Research Corporation

project number:
FE0032129

predecessor projects:
N/A

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partners:
Oak Ridge National Laboratory (ORNL);
ReactWell LLC;
Trimeric Corporation

start date:
10.01.2021

percent complete:
17%

features, at a minimum: (i) a tapered air intake to reduce pressure drop related to entrance effects; (ii) a structured network of heat transfer channels to enable localized cooling and heating during adsorption and desorption, respectively; and (iii) low pressure drop supports for the fiber sorbents (Figure 1). This hybrid manufacturing approach provides a facile method for taking fiber sorbents from lab scale to pilot scale as it dramatically simplifies the fabrication of heat-integrated contactor structures.

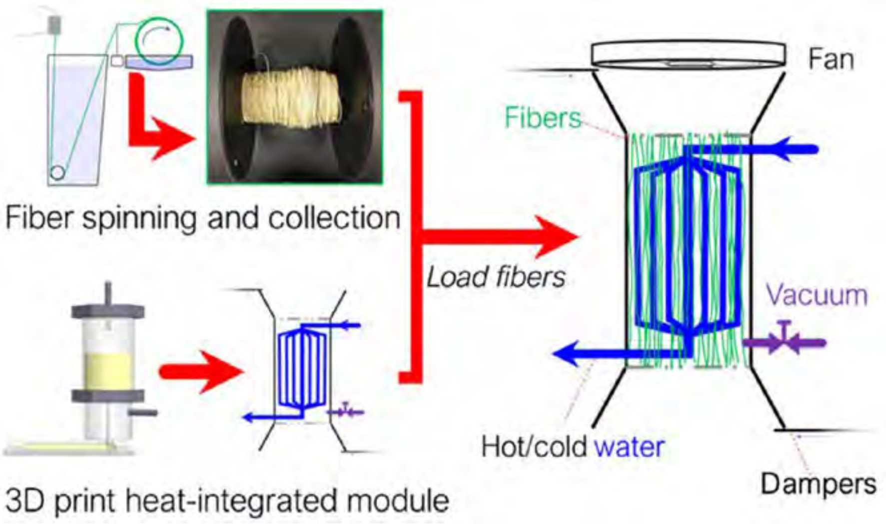

Figure 1: Schematic of proposed technology. The scalability of fiber sorbent spinning (top) is leveraged via novel 3D-printed contactors with internal heating and cooling elements (bottom). The fibers are easily loaded into the contactor without need of glue or epoxy, simplifying manufacturing and driving down costs (right).

This combination of fiber sorbent spinning, re-infusible polyamines, and 3D-printed modular housing provides several advantages that accelerate the translation of DAC materials out of the lab and into the field. Three scalable and modular components are combined into a system that is straightforward to build: (i) the contactor, which provides mechanisms for delivering air, removing/adding heat, and enabling vacuum; (ii) the fiber support, which provides high surface areas and low pressure drops via fiber alignment; and (iii) the active amine adsorbent that is infused into the fiber post-spinning, which enables geography-specific customization in terms of the amine composition and loading. Key challenges in the fabrication of heat-integrated hollow fiber sorbents are avoided, as are difficulties associated with 3D-printing high integrated module devices. Indeed, decoupling the adsorption contactor into two components (the fiber and the novel housing) captures advantages of an all-fiber or an all-3D-printed contactor, but with significant improvements in scalability.

The goal is to create a contactor platform that enables reductions in DAC CO_2 costs to \$100/tonne CO_2. Initial pre-screen TEA estimates from the project team suggests that a pathway to \$100/tonne exists (Figure 2). There are three major cost barriers that are often associated with DAC systems: the fans, the sorbent, and the heat input. Fan costs can be reduced via the creation of low pressure drop structures, which is an objective of this proposal. The sorbent costs can be reduced by rapidly cycling the adsorption system; beyond this, using commodity-scale materials wherever possible and ensuring that the materials have a lifetime of at least one year can further drive down costs. Both of these approaches are being pursued over the course of this project. The final major cost associated with DAC systems is the energy input to desorb the captured CO_2. These are ultimately bounded by the sorption or reaction enthalpy of the adsorbate-adsorbent systems. In the case of heating-induced desorption, avoiding losses associated with poor heat transfer, high thermal masses of contactor materials, and other inefficiencies can reduce the energetic requirements for the CO_2 desorption step. Monoliths are solid contactors composed of parallel channels resembling a honeycomb structure. Monoliths have several advantages over packed beds, such as higher mass transfer rates, good attrition properties, and lower pressure drop, but this is typically balanced against a lower loading of sorbent per unit volume. Monoliths can either be made entirely of the sorbent material, as when the sorbent material is directly extruded with no binder, or with some fraction of sorbent dependent on ratios of binder/sorbent/monolith body, as is the case with many deposition or growth methods (the latter is most common). Laminate-style contactors are essentially simpler forms of monoliths comprised of 1D slits. However, laminates are difficult to make reproducibly. The precision in manufacturing must be quite high to avoid slit bypass effects (less than 5% differences in channel size is required for uniform flow). This level of precision is difficult to scale, and thus laminate-style adsorbents are not often used in gas-separation processes. From a scalability perspective, monoliths are essentially made from high-quality ceramic materials one at a time using high-precision, multi-step robotic equipment.

This process has been commercialized, but the fundamentals of processing ceramics suggest that upper limits on manufacturing rates are being reached and that these rates are likely too low to drive down adsorption contactor costs by an order of magnitude.

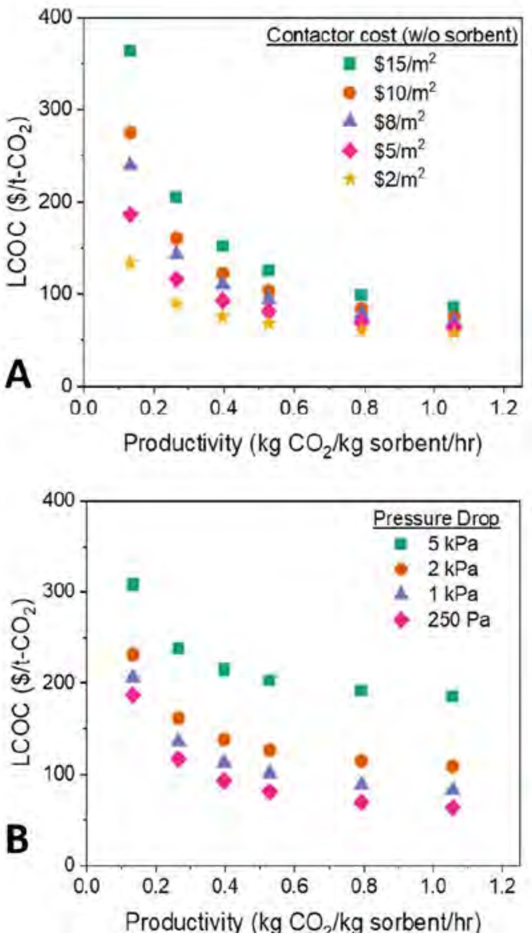

Figure 2: Pre-screen TEA results. Levelized cost of CO_2 capture as a function of productivity and (A) contactor cost or (B) pressure drop. Other parameters are held constant, including one-year sorbent lifetime, -65 kJ/mol heat of adsorption, 300 seconds cycle time, and 100,000 tonne CO_2/year captured.

The project team initially developed polymeric hollow fiber contactors that supported high loadings of CO_2 adsorbents. These materials are highly scalable and facilitated heat-integrated process configurations for post-combustion CO_2 capture. These "hollow fiber sorbents" have several important features that provide solutions to deleterious issues typically associated with post-combustion CO_2, and these solutions have proven to be transferrable to DAC technologies. For instance, CA fiber sorbents containing mesoporous silica impregnated with polymeric amines have been previously developed for DAC applications. In the case of fiber sorbents, the polymeric amines are added to the fibers in a simple, scalable post-spinning infusion step. The porous fiber support allows rapid gas access to the high loadings (~60 wt%) of sorbent particles within the fiber wall. Moreover, the fibers themselves act as structured packing elements, thus allowing for low gas pressure drops (~0.1 pounds per square inch [psi]/foot; Figure 3). This prior work demonstrated the ease at which these materials can be made in large quantities (400 g–1 kg scale per day), and desorption experiments highlighted the ability of these fibers to create CO_2 products that have purities in excess of 98 mol%. The adsorption and desorption chemistry, kinetics, and thermodynamics of the PEI-infused CA/silica sorbents are well understood. Carbon dioxide chemically binds to the PEI located in the silica pores within the CA matrix, and a temperature vacuum swing can be used to desorb the CO_2.

Traditionally, a dense barrier layer is installed on the bore-side of fiber sorbents, preventing mass transport from the shell side of the fibers to the bore, transforming the fibers into integrated "adsorbing heat exchangers." The fibers are capable of rapid thermal cycles on the order of one to four minutes and have excellent heat management properties (Figure 4). However, the barrier layer addition is the most time-intensive and tedious step of the fiber sorbent fabrication process and prone to defect formation. The contactors proposed here entirely eliminate the need for a barrier layer through advanced 3D-printing technology, thus reducing the time, complexity, and fragility of the contactor manufacturing and assembly process.

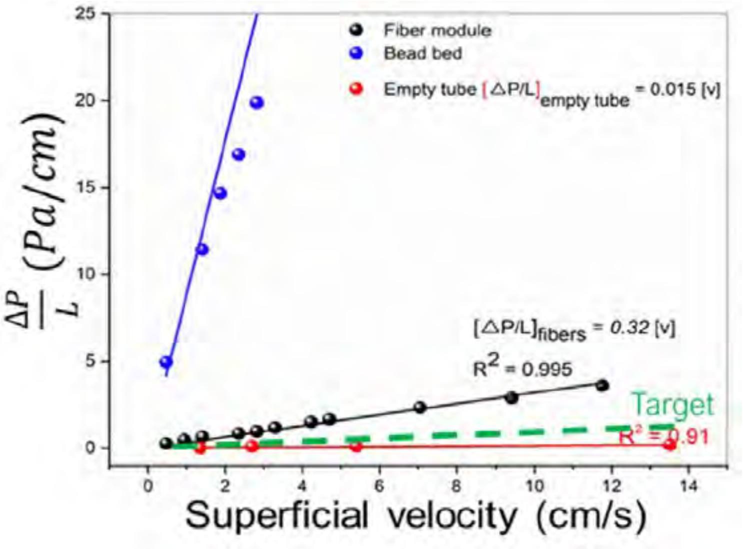

Figure 3: Pressure drop comparison and targets. Target pressure drop for this work is 250 Pa at 3 m/s air speed and is shown by the green line.

In recent years, 3D printing has been used as a method to directly print sorbent-containing monoliths. However, creating internal porosity inside the polymer-adsorbent structure and maintaining high sorbent loadings is a complex task, and the technology is further from scale-up than fiber sorbents. Importantly, printing commercially available polymers is a technologically mature process that has already been scaled up. By hybridizing fiber sorbents and 3D-printed contactors, the most complex aspects of each technology (barrier layer addition of fiber sorbents and internal porosity of 3D printing) are eliminated. Other limitations, including entrance pressure drop, sorbent degradation from direct steam contact, and low productivity due to inefficient heat management, can also be overcome via contactor design.

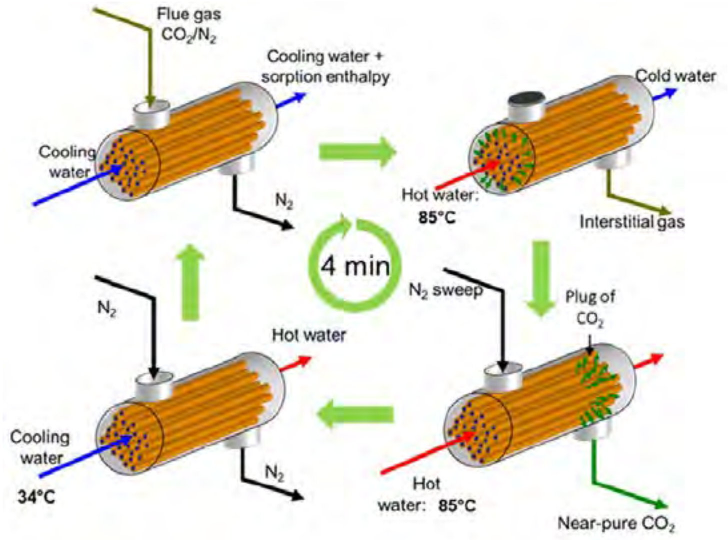

Figure 4: Rapid thermal swing adsorption cycle originally demonstrated for post-combustion CO_2 capture. Cycle times of 2.5–4.0 minutes have been demonstrated experimentally for 10% CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	—	—
Average Particle Diameter	mm	—	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Attrition Index	-	—	—
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	\$/kg	\$3.00	\$1.50
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	22°C	22°C
Equilibrium Loading	g mol CO_2/kg	1.2	1.4
Heat of Adsorption	kJ/mol CO_2	-65	-65
CO_2 Adsorption Kinetics	gmol/time	—	—
Desorption			
Pressure	bar	0.003 bar CO_2	0.3 bar CO_2
Temperature	°C	110°C	80°C
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.1	0.2
Heat of Desorption	kJ/mol CO_2	65	65
CO_2 Desorption Kinetics	gmol/time	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	laminate or shell-tube	
Flue Gas Flowrate	kg/hr	—	
Space Velocity	hr^{-1}	60000	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	1.25	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— N/A ; 95%, 0.003 50%, 95%, 0.3	—
Adsorber Pressure Drop	bar	1000 Pa	<500 Pa
Degradation	% capacity fade/cycle	0.1	0.0005
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Composition						
	vol%					ppmv	
	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	>300	100-150—
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	—	—
Operating Expenditures	\$/tonne CO_2	—	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

technology advantages

- High sorbents loading in hybrid fibers reduces cycle time.
- Low pressure drop design.
- 3D hybrid fibers are easy to manufacture and assemble, making these suitable for large-scale production.
- Reduce material costs and regeneration heat duty via the use of all-plastic components.

R&D challenges

- Develop sorbent with half-life target equal to one year via non-oxidative internal cooling.

status

GTRC is currently working on fiber fabrication, weaving, and integration into DAC contactors. Fiber bed and woven laminate modeling and validation work are also underway. The design and 3D-printed structure models of the shell-and-tube and plate-and-frame designs are also being developed.

available reports/technical papers/presentations

Ryan P. Lively, David S. Sholl, Matthew J. Realff, Joshua A. Thompson, Anne I. Ryan, Brandon J. Iglesias, “Hybridizing Heat-Integrated 3D Printed Modules with Mass Manufacturable, Low Pressure Drop Fiber Sorbents,” Project kickoff meeting presentation, Pittsburgh, PA, December 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12554&filename=Hybridizing+Heat-Integrated+3D+Printed+Modules+with+Mass+Manufacturable%2c+Low+Pressure+Drop+Fiber+Sorbents.pdf*.

Electrochemically Regenerated Solvent for Direct Air Capture with Co-Generation of Hydrogen at Bench Scale

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER), Vanderbilt University, the Electric Power Research Institute (EPRI), and Louisville Gas and Electricity and Kentucky Utilities (LG&E and KU) are developing an intensified, cost-effective, and easily scalable process using aqueous potassium hydroxide (KOH) as a solvent for direct air capture (DAC). The process features the use of a hybrid membrane absorber (MA) coupled with an electrochemical solvent regenerator (ER) that is capable of extracting carbon dioxide (CO_2) from the atmosphere and pre-concentrating KOH solvent followed by regenerating the solvent to release CO_2 in the ER, and simultaneously refreshing the capture solvent while producing hydrogen (H_2) to offset the DAC cost.

technical goals

- Design and fabricate a hybrid bench-scale MA and ER with suitable electrode material and the flow channel pattern.
- Perform system integration, installation, and commissioning (EPRI and UK CAER).
- Pursue parametric studies of the bench-scale system through long-term operation, focusing on:
    1. Performance of the MA with a focus on CO_2 capture efficiency, gaseous pressure drop, and gas-liquid contact effectiveness (UK CAER and Vanderbilt).
    2. Performance of the ER with the target of minimizing both the operating voltage and H^+ transport through the cation-exchange membrane (UK CAER).
    3. Leveraging long-term operation to investigate the degradation mechanisms of both the electrode and membrane materials (UK CAER).
- Develop a techno-economic assessment (TEA) and life cycle analysis (LCA) to compare against commercial technologies (EPRI).

technical content

The two-unit operation employs a hybrid MA that extracts CO_2 from air, enriching carbon content in the solvent solution after capture, coupled with an ER that releases the CO_2 and simultaneously produces H_2 as a saleable byproduct. The process operates in a loop with a chemically stable and non-toxic potassium (K+) solvent that offers both fast absorption kinetics and near-zero vapor pressure. The system in Figure 1 shows: (1) a hybrid MA to capture CO_2 from the atmosphere to form carbonate (CO_3^{2-}), and (2) an ER to regenerate hydroxide (OH^-) while producing H_2 at the negative chamber.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Novel Concepts

project focus:
Hybrid Membrane Absorber Coupled with Electrochemical Solvent Regenerator for DAC

participant:
University of Kentucky

project number:
FE0032125

predecessor projects:
N/A

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partners:
Electric Power Research Institute; Vanderbilt University

start date:
10.01.2021

percent complete:
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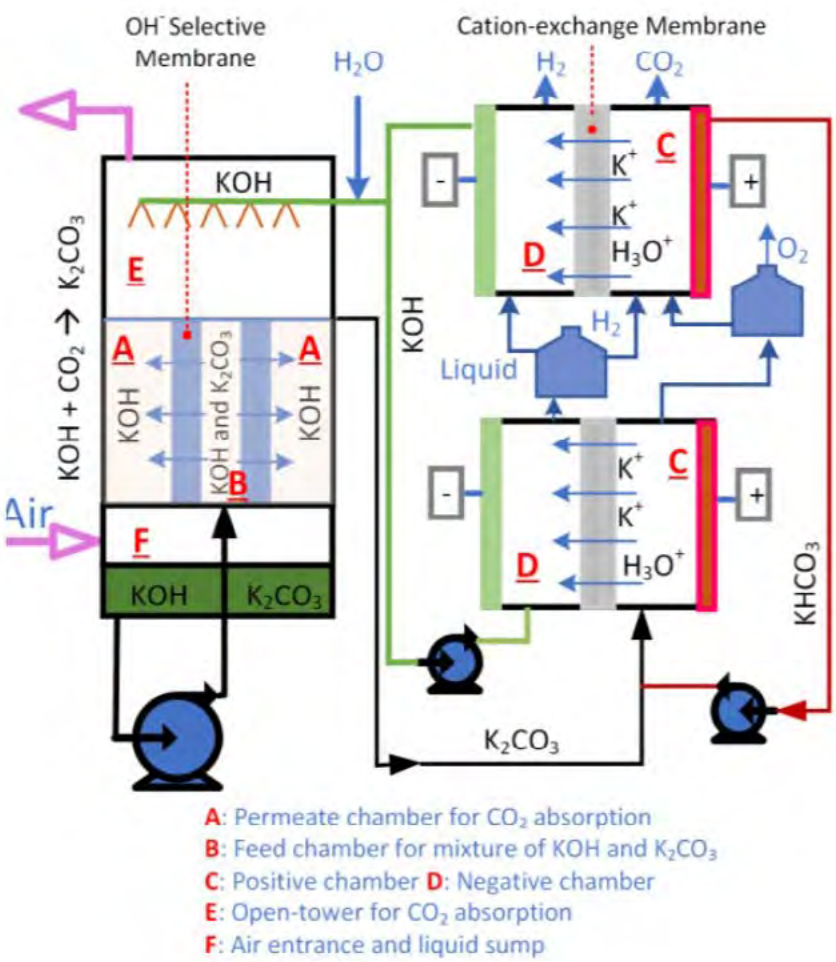

Figure 1: University of Kentucky Research Foundation (UKRF) solvent–based DAC process.

Key features of the process include: (1) utilizing dilute KOH as the capture solvent in a compact hybrid absorber; (2) using an OH^- selective nanofiltration membrane to concentrate carbon content in the rich solvent prior to regeneration to reduce the parasitic reactions; (3) producing saleable H_2 to offset the CO_2 capture cost; and (4) leveraging the mature technologies of nanofiltration and the alkaline electrolyzer to make the process easily scalable.

In addition to the solvent spray at the open tower (E) for CO_2 capture and air entrance above the liquid sump (F), the middle of MA has two chambers divided by an OH^- selective membrane acting as structured packing for gas-liquid contact, in which, at the permeate chamber (A) with large cross-section area (to maintain the gas velocity below 1.5 m/s) under ambient conditions, CO_2 from air is effectively captured using a 2~5 wt% KOH liquid. The majority of CO_2 is captured in the open tower section, while the wetted membrane surface provides the additional gas-liquid interface for reactions to boost the carbon loading. At the feed chamber (B) under a moderate operating pressure (e.g., less than 200 pounds per square inch gauge [psig]), K_2CO_3 collected from the prior CO_2 capture process from the sump is separated from the unreacted KOH. Furthermore, similar to a conventional alkaline electrolyzer, the ER is a compact electrochemical cell equipped with an ion-exchange membrane and catalytic positive and negative electrodes. At the chamber with the positive electrode, CO_2 gets liberated, and at the chamber with the negative electrode, H_2 gas is produced via typical water electrolysis.

As shown in Figure 1, the UK CAER process in brief, aqueous KOH produced from the negative chamber of the ER (D) enters the open tower of the MA from the top via liquid spray while air enters near the sump. Under such a countercurrent configuration, KOH reacts extensively with CO_2 from air to form K_2CO_3 via $2KOH + CO_2 = K_2CO_3 + H_2O$ under ambient pressure in the open tower, along with the permeated KOH in permeate chamber (A) flowing downward against the membrane surface. Subsequently, the unreacted KOH and K_2CO_3 are transferred from the sump to the feed chamber of the membrane, where the KOH gets selectively transported across the OH- selective membrane, leading to the purified CO_3^{2-} solution (e.g., K_2CO_3) prior to regeneration in the ER. The K_2CO_3 resulting from the MA is first pumped to the positive chamber (C) of the ER, in which CO_3^{2-} is converted to carbon dioxide (CO_2) via three-step reactions of 4OH- +

4e- = O_2 + $2H_2O$, CO_3^{2-} + H^+ = HCO_3^- followed by HCO_3^- + H^+ = CO_2 + H_2O. Meanwhile, K^+ is repulsed by electrostatic forces through the K^+ selective membrane to the negative chamber (D) to balance the electronic charge along with a portion of H^+. At the negative chamber with the liquid recirculation, H_2 is produced via $2H_2O$ + 2e- = H_2 + $2OH^-$ while forming KOH for the next CO_2 capture cycle in the MA. In the UK CAER process, the concentration of the K+-based solvent is adjustable with internal recirculation and make-up water (H_2O) to satisfy both the CO_2 capture performance in the MA and operating voltage for the ERs.

To produce a high-purity CO_2 stream, a two-stage ER is utilized in which two ERs with the same physical structure and functionality are connected in series. The bottom ER converts aqueous CO_3^{2-} to HCO_3^- and releases O_2 in the positive chamber. The HCO_3^- solution can then be flashed for CO_2 release or H_2 released in the negative chamber of the bottom ER is purged into the liquid fed to the positive chamber in the top ER, thereby biasing the positive electrode. Under such configuration, in the top ER, O_2 evolution at the positive chamber can be minimized via depolarization technique to facilitate the acidification process of $KHCO_3$ via HCO_3^- + H^+ = CO_2 + H_2O towards producing high-purity CO_2.

Process Features:

(1) Hybrid membrane absorber for CO_2 capture using diluted KOH solution. The low CO_2 concentration in air generates a significant challenge on the gas/liquid contact surface if a concentrated KOH solution is used. Compared to a liquid/gas mass ratio of 1 for the application of 5 M solvent to capture CO_2 from natural gas combustion flue gas (~4 vol% CO_2), applying the same solvent for air capture (~0.04 vol% CO_2) will result in the liquid/gas mass ratio as low as 0.01, which is too low to produce effective gas-liquid contact interface on any commercially available packing. One effective way to solve the challenge is to use the diluted solvent (e.g., 0.5–1 M). However, the lower the solvent concentration, the higher energy needed to regenerate the solvent after capturing CO_2. The hybrid MA (a) effectively absorbs CO_2 via spraying the solvent onto the mist in the open-tower, thereby reducing the overall capital cost of the absorber while enhancing CO_2 capture by hydroxide permeate on the membrane surface; and (b) reduces parasitic reactions by removing OH- and pre-concentrating the capture solution's carbon content for the ER. The removal of OH^- prior to the solvent regeneration at the ER bottom eliminates the electron/charge transfer spent on the parasitic KOH neutralization toward non-CO_2 liberation at the positive chamber of the ER. For instance, when KOH enters the positive chamber of the ER, H+ reacts with OH- forming H_2O; in contrast, when K_2CO_3 enters the positive chamber of the ER, H+ reacts with CO_3^{2-} leading to the CO_2 product.

(2) Besides producing KOH as a highly effective CO_2 capture solvent, the ER can simultaneously generate ≥99.9% purity H_2 as a saleable carbon-free energy carrier, thereby offsetting the overall DAC process cost. In the proposed process, H_2 is produced at the negative chamber of the ER by accepting two electrons while liberating CO_2 at the positive chamber of the ER by giving away two electrons to produce H+, which means that for each mole of CO_2 captured from air, one mole of H_2 coproduct is produced through electrolysis. Furthermore, since H_2O is the only electrochemical active species at the negative chamber of the ER, 100% of electronic charge efficiency is expected toward H_2 production. In addition, internally recirculating the liquids help retain a high level of ionized species, therefore stabilizing the ER's overall electrical conductivity. Such an operating configuration will further lead to H_2 production at a reliable operating voltage, thereby mitigating the voltage variation, which may be detrimental to the equipment lifespan.

(3) The proposed process is easily scalable to a larger scale, as both the MA and ER are built upon mature technologies. The MA is built upon liquid atomization and the nanofiltration technology, utilizing the membrane with either enhanced chemical surface charge or size-exclusion to selectively separate monovalent ions from divalent ions under a moderate operating pressure. For this case, OH- is separated from CO_3^{2-}. Moreover, the design of the MA will leverage the physical structure of the commercialized membrane contactors and spray towers, thereby providing a convenient pathway for modulation. The ER in the proposed process is slightly modified with respect to the conventional alkaline electrolyte. For this case, instead of using an anion-exchange membrane, a cation-exchange membrane is utilized to attain a high quality of KOH for efficient CO_2 capture from air while producing H_2.

In this project, the team is designing and fabricating a bench-scale unit (up to 10 cubic feet per minute air flowrate) and conducting parametric and long-term studies to inform next-scale process development.

TABLE 1: PROCESS PARAMETERS

Performance Attributes	Units	Current R&D Value	Target R&D Value
Carbonate Rejection/Hydroxide Rejection	%/%	50/<10	80/<10
Nanofiltration Membrane Fade	%/hr	N/A	0.02
ER K^+ Transport Efficiency	%	65	80
Membrane K^+ Transport Fade	%/hr	0.06	0.02
CO_2 Capture Efficiency	%	60	>90
Space Velocity	Hr^{-1}	1200	3600
Pressure Drop	Pa	N/A	1000
Regenerator Operating Potential	Volts	4	2.7
Regeneration Energy (55% thermal/electric)	kJ/mole	880	600
Overall Volumetric Productivity	gmol CO_2/ hr	0.001	2

Definitions:

Absorber Geometry – Hybrid absorber integrating nanofiltration stacking and liquid atomization in open tower architecture.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	68-72°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

CO_2 Capture Mechanism – The driving force for capture is the partial pressure difference between CO_2 in air and the capture solvent on the nanofiltration face and in the open tower section. The electrochemical cell regenerates the solvent after CO_2 is absorbed to preserve the driving force.

Flue Gas Pretreatment Requirements – N/A

Product Streams Generated – Hydrogen for sale.

Process Design Concept – See Figure 1.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	541	<200

Definitions:

Cost of Carbon Captured – The capture cost is estimated assuming ~4 V operation of the electrochemical regenerator, regenerator cost is >80% capture cost, 10 cents/kWh electricity cost.

technology advantages

- The proposed process is easily scalable to a large-scale, as both the MA and ER are built upon mature technologies.
- Simplified (two-unit operation) capture process with a significant reduction (greater than 25%) in both the capital and operating cost while producing H_2 as a saleable byproduct.
- Provide easy integration with renewable power sources for remote operation and reducing carbon emissions.

R&D challenges

- Design of anode-cathode to minimize voltage loss due to sluggish kinetics.
- Design of flow channel for rapid degassing.

status

UK CAER has begun designing and fabricating the CO_2 capture technology consisting of a hybrid MA that extracts CO_2 from air, enriching carbon content in the solution after capture, coupled with an ER for solvent regeneration. UK CAER is currently performing parametric evaluation for membrane integrity, transmembrane pressure, and OH^-/CO_3^{2-} selectivity for the MA, as well as cell development for the ER.

available reports/technical papers/presentations

Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," Project kickoff meeting presentation, November 20121. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12447&filename=Electrochemically+Regenerated+Solvent+for+Direct+Air+Capture+with+Cogeneration+of+Hydrogen+at+Bench-Scale.pdf*.

Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of Carbon Dioxide

primary project goal

Harvard University is conducting experimental verification of a novel approach for direct air capture (DAC) of carbon dioxide (CO_2) that employs an alkalinity concentration swing (ACS) process. ACS involves concentrating an aqueous alkaline solution (that has equilibrated with air) using commercially available technologies such as reverse osmosis (RO) or capacitive deionization (CDI). The concentrated solution has a higher partial pressure of CO_2 relative to the initial solution, allowing the CO_2 to be separated and stored.

technical goals

- Adapt the design of RO and CDI from their traditional desalination uses and tune each for a specific target concentration factor (10-times for RO; 100-times for CDI) necessary to extract CO_2 from alkaline solution.
- Assemble a calibrated system to measure CO_2 extracted from solution and build a subsystem to extract CO_2 from concentrated solution using either a vacuum on a fluid reservoir and/or using gas permeable membrane technology.
- Use CO_2 measurement and extraction systems to test the solution's equilibrium and kinetic properties key to the ACS, including how dilution and re-equilibration with air proceed.
- Demonstrate system integration and energy quantification coupled to the ability to extract CO_2 from solution concentrated by RO or CDI and measure the energy necessary to operate the process per quantity of CO_2 captured.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

The concentration of dissolved inorganic carbon (DIC)—the sum of carbonate ion, bicarbonate ion, and dissolved CO_2—in equilibrium with air ($pCO_2 \approx 415$ parts per million [ppm]) depends on the alkalinity of a solution (i.e., the charge difference between the sum of the conservative cations and anions in solution). As the alkalinity of a solution increases, the amount of DIC, when equilibrated with air, increases, but at a decreasing rate. This is due to the transition from bicarbonate as the dominant species of DIC (at an intermediate pH range from 6.5–10) to carbonate ion as pH increases. At higher alkalinity and higher pH, the charge balance required is now accommodated primarily by carbonate ions, which are divalent. Consider any basic solution in equilibrium with air—if pure water is removed from this solution in a closed system with respect to the dissolved components (including CO_2), both the DIC and the alkalinity increase in proportion to their relative concentrations in the solution, while the partial pressure of CO_2 steadily increases, due to the change in speciation of carbon from bicarbonate to carbonate. This creates an opportunity for collection of CO_2 in concentrated form. The solution can be recycled simply by recombining the concentrated solution with the freshwater produced from the RO or CDI modules and then allowing it to re-

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Solvents

project focus:
Alkaline Concentration Swing Process for DAC

participant:
Harvard University

project number:
FE0031964

predecessor projects:
N/A

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partners:
N/A

start date:
02.09.2021

percent complete:
50%

equilibrate with air, returning the system to the initial point. The cycle is illustrated in Figure 1, which shows the first two steps (concentration and outgassing) of the ACS.

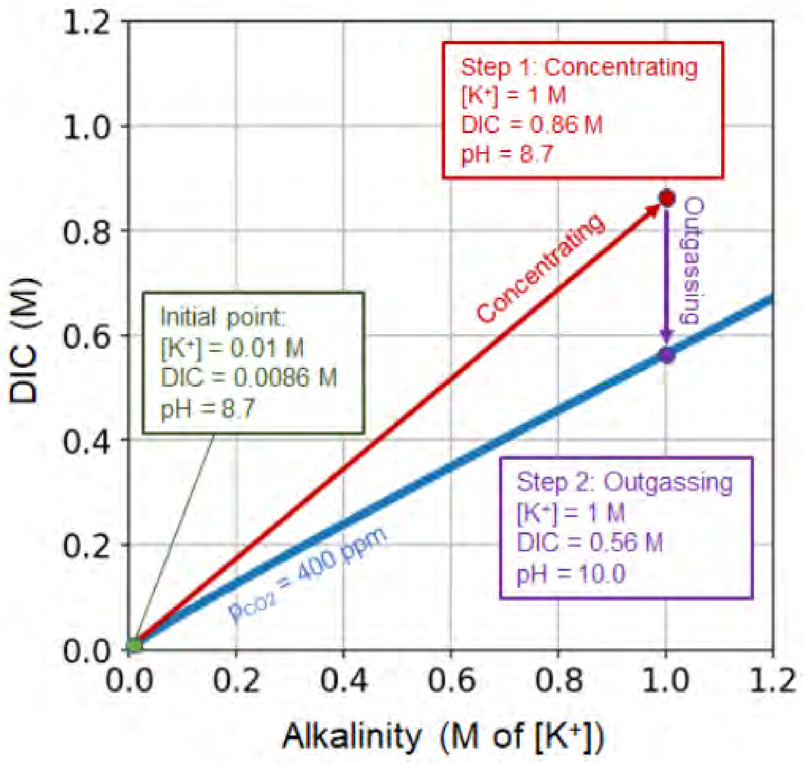

Figure 1. The ACS cycle (concentrating and outgassing steps).

Figure 1 plots a representative example of a solution at 0.01 M alkalinity (K+), equilibrated at pCO_2 of 400 ppm, concentrated by a factor of 100 to 1 M alkalinity. At these values, the solution will outgas 3 mM of CO_2 with respect to the feed. In Figure 1, the blue line plots the relationship between DIC concentration at a fixed partial pressure of CO_2 (400 ppm) as a function of alkalinity. The red arrow indicates the concentration step of the ACS and plots the trajectory in DIC and alkalinity space if a solution that was equilibrated at 0.01 M alkalinity (green point) was concentrated by a factor of 100 times to an alkalinity of 1 M. In the concentrated state (red point), the solution has an excess DIC to the amount of alkalinity in solution. When exposed to a pressure of 400 ppm, the purple arrow indicates the amount of CO_2 that would outgas as the system reaches a new equilibrium at high alkalinity. This figure does not show the remaining step of the ACS, dilution and atmospheric CO_2 re-equilibration, which would return the system to the initial point.

This basic approach will work with any strong base. Potassium hydroxide solutions are the solvent of choice due to the very high solubility of potassium bicarbonate. Sodium bicarbonate is less soluble, and the concentration step may drive precipitation of solids, which would complicate the process; calcium carbonate is even less soluble. There are multiple tradeoffs to consider in terms of what concentrations to use for optimization of the ACS process. Starting with more dilute solutions (e.g., 0.01 M), and then concentrating by a factor of 100, can produce a higher CO_2 outgassing pressure from the concentrated solution, but requires more energy for the concentration step and a larger initial feed solution volume. On the other hand, starting with a more concentrated initial solution (e.g., 0.6 M) can result in a significantly lower ACS energy requirement and, at this higher initial alkalinity, ingassing kinetics (i.e., re-equilibration with air following dilution) are also significantly faster, based on estimates using the literature.

It is difficult to make detailed calculations of the energy demand of DAC without experimental demonstration of the full cycle as is being performed in this project. However, using standard numbers for energy use in RO desalination plants and at similar concentration ranges, a rough estimate of 1.7 megawatt-hours (MWh) of electricity per tonne of CO_2 was obtained, which suggests there is potential for improvement on the 2.28-MWh minimum energy requirement in published estimates of solvent-based DAC energy requirements. Another important advantage of the ACS approach to DAC is that, because it makes use of existing technologies for water purification and desalination that are widely deployed at commercial scale around the world (such as RO), the capital costs of this approach to DAC are likely to be extremely low. High capital approaches to DAC require steady power supply and continuous operation to reduce costs; ACS has the potential to harness very inexpensive but intermittent energy sources (such as wind) that would be impossible if capital costs for the system were high.

This project's approach to experimental demonstration of ACS is to first test each step of the system independently before integrating them into a full cycle. The process has been divided into three subsystems (shown in Figure 2).

1. Concentration of an alkaline solution.
2. Carbon dioxide extraction.
3. Dilution and re-equilibration with air.

For the concentration step, which is at the heart of the ACS process, the project team is conducting experiments on two parallel approaches. First, to use a laboratory-scale RO desalination system; second, to use a CDI system that has advantages at lower concentration ranges. One experimental range of concentrations for the ACS is being used in both systems to allow for direct comparisons. Two approaches for CO_2 extraction—one applying a vacuum on a fluid reservoir and another making use of gas permeable membrane technology are also being evaluated.

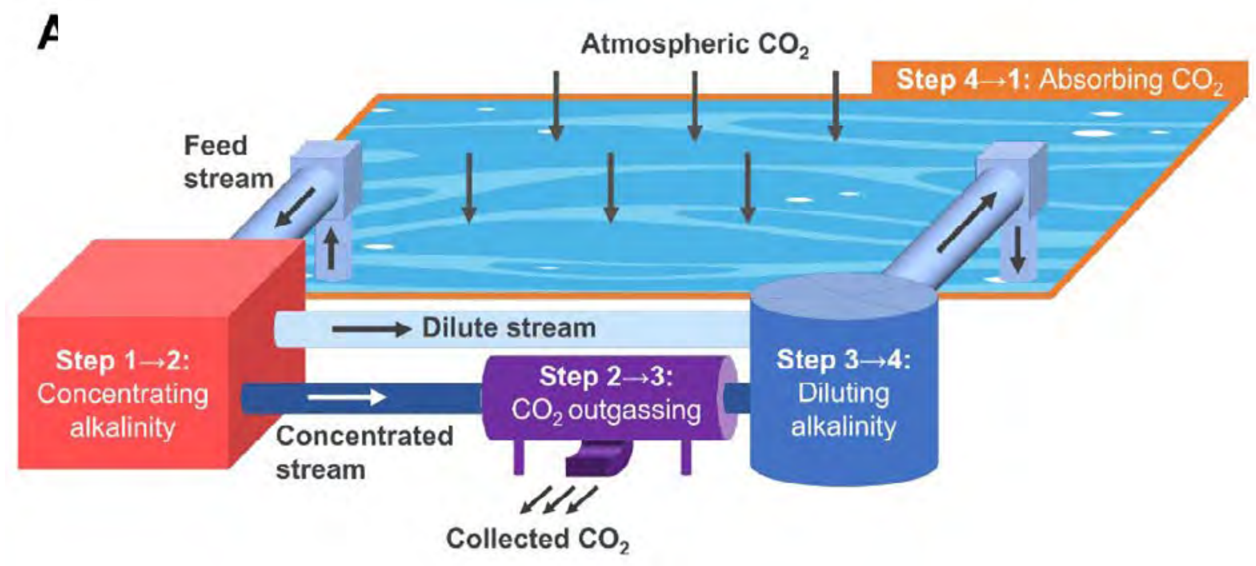

Figure 2. System schematic for ACS implementation. (A) Flow diagram indicating the three steps of the ACS: (1) concentration; (2) CO_2 extraction; (3) dilution and re-equilibration with air.

Concentration Step Using RO

RO is a membrane-based separation process where pressure is applied against a solvent-filled solution, overcoming the solution's osmotic pressure, to create a concentrated and purified stream. RO technology has a wide range of applications, from wastewater treatment and home water purification to seawater desalination. Desalination plants are designed to produce a stream of freshwater from an input feed of about 0.6 M of sodium chloride (NaCl)-equivalent salt (i.e., seawater), yielding a brine of roughly double the original salinity. This exact process can be used to demonstrate the carbon capture approach of the ACS, but different membranes need to be tested, in particular with respect to rejection of DIC and the alkalinity carrier (K+), as well as water permeability—both factors that contribute to the maximum reachable concentration factor. Unlike in traditional desalination processes, higher permeability may be tolerated since minimizing the salinity of the permeate stream is not a necessary optimization goal for the ACS. Initially, a range of commercially available polyamide thin-film composite membranes and cellulose acetate membranes are being tested, deploying different membrane performance parameters testing salt rejection between 95–99% and permeabilities between 28.9–68 L/m^2/h, over a range of applied pressures, between 5–80 bar. In order to reach higher concentration factors, more advanced membrane geometries, such as spiral-wound membranes, could be tested to increase the surface area of the membrane in the RO cell. The RO module used in this experimental system consists of two main components: the pressure pump driving the alkaline feed solution and the RO cell. Prior to the integration of all three subsystems, the initial feed solution will be a 0.6-M potassium hydroxide solution equilibrated with air by bubbling air with a controlled CO_2 partial pressure through a reservoir. The pressure pump can reach up to 80 bar (typical seawater desalination pressures), allowing for an osmotic separation of more than 1 M of NaCl equivalent ions across the RO membrane and reaching a concentration factor of 2. A lower feed concentration of 0.1 M—concentrated by a factor of 10 reaching 1 M—is also being tested and compared to CDI experiments.

Concentration Step Using CDI

CDI provides an alternative mechanism for concentrating the alkaline solution. CDI is a method of concentrating and removing anions and cations from solution by applying voltage across two electrodes, adsorbing anions to the positive electrode and cations to the negative electrode to dilute the solution. When the voltage is switched off, the release of the adsorbed ions creates a high-alkalinity brine, which constitutes the concentrating step of the ACS.

CDI systems operate best in brackish water conditions, with salt concentrations below 200 mM, and early-stage CDI systems have been commercialized for desalination, wastewater remediation, and water softening. The effective operation of CDI in this range makes it a candidate for optimal implementation of the ACS at lower salinity. The ability to work at lower initial concentrations enables larger concentration swings that have a larger yield and can thus result in significantly lower energies per unit CO_2 outgassed, as shown in Figure 1. Furthermore, CDI may enable outgassing directly within the concentration module, using gas diffusion electrodes, providing an option for continuous cycling by avoiding the need for a separate outgassing chamber.

Unlike RO systems, commercial CDI systems are less mature and are not designed to be gas-tight, so most commercially available systems are not appropriate for experiments. Because CDI systems do not require high pressure for operation, it is straightforward to create customized test cells at the lab scale and at relatively low cost. The CDI module, at its most basic, consists of a chamber in which the alkaline, air-equilibrated feed solution can come into contact with two electrodes. A type of “sandwich" CDI device is being used, in a “flow-by” configuration, to allow for continuous cycling and reproducible experiments with controllable electrode size, surface area, and cell geometries.

System Integration: Full Demonstration of ACS Cycle

After independently testing each of the three components of the ACS approach—(1) concentration of an alkaline solution, (2) CO_2 extraction, and (3) dilution and re-equilibration with air—the combined system can be tested to demonstrate the full ACS cycle. Testing of the full system involves verifying that the carbon removed by the integrated system matches the predicted values for each swing from the theoretical ACS predictions. The energy required for each swing is also measured to determine an overall energy requirement per mole of captured CO_2. This integration of the three modular components of the experimental system achieves a Technology Readiness Level (TRL) of 3. Based on estimates of the energy requirement for RO in standard saltwater conditions, estimates suggest the ability to achieve CO_2 capture at an energy below 2.0 MWh per tonne of captured CO_2 (265 kilojoule [kJ]/mol). Beyond TRL 3, this requirement could be improved upon by implementing pressure-retarded osmosis, enabling energy recovery when concentrated and diluted solution streams are recombined. Based on estimates of the energy requirement for CDI in standard brackish water conditions, it is estimated to achieve CO_2 capture at an energy of 1.9 MWh per tonne of captured CO_2 (300 kJ/mol). Because electricity flows in the reverse direction when the electrodes are switched off, CDI enables energy recovery; the literature commonly reports energy recovery of 50%, with some studies approaching 80%. However, there is no specific energy target required to achieve TRL 3.

technology advantages

- Process utilizes well-established, commercially available technologies, including RO and CDI.
- In the RO method, higher feed concentration outgasses more CO_2 for the same concentration factor and higher concentration factor outgasses more CO_2 for the same feed concentration.

R&D challenges

- Assembling a crossflow RO system.
- Prototyping CDI cells with a larger electrode mass-to-cell volume ratio.
- Building a fully operational CDI model with small volume handling.
- Implementing bicarbonate selectivity with anion exchange membranes.
- Assembling an integrated system and conducting a full demonstration of the ACS cycle.

status

Harvard University has developed and assembled a dead-end RO system and achieved operating conditions comparable to published systems. Current efforts involve assembling crossflow RO systems and performing kinetic modeling of the experimental results. Researchers have also assembled the CDI system and the initial experimental work indicated operation is comparable to published brackish water CDI systems. Their CDI experiments revealed that higher initial concentrations do not yield larger current or overall capacitance; that higher flow rate, spacer thickness, and cell compression all improve the cell operation; and that a fluid handling system for moving and measuring small volumes is necessary for detecting high concentration factors. Current efforts involve completion of testing the process subsystems and construction of the integrated ACS system.

available reports/technical papers/presentations

Daniel P. Schrag, Michael J. Aziz, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO_2," Direct Air Project kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Schrag.pdf*.

Daniel P. Schrag, Michael J. Aziz, Andrew Bergman, Anatoly Rinberg, "Experimental Demonstration of Alkalinity Concentration Swing for Direct Air Capture of CO_2," kickoff meeting presentation, Pittsburgh, PA, November 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=12414&filename=Experimental+Demonstration+of+Alkalinity+Concentration+Swing+for+Direct+Air+Capture+of+CO2.pdf*.

Novel, Efficient Contactor Technology to Substantially Lower the Cost of Direct Air Capture of CO_2

primary project goal

During the Phase I project, Emissol LLC designed, modeled, prototyped, and tested a novel honeycomb contactor smaller than typical honeycomb contactors. The contactor was rigorously tested both experimentally and in mathematical models. Good agreement was observed between the project's test data and math-modeling results. It was observed that the novel contactor captures and removes carbon dioxide (CO_2) at a high rate while also requiring approximately 40% less sorbent than typical honeycomb contactors. This was a significant finding, as for many DAC systems the sorbent cost could be 80–85% of the total capture cost.[1] Given the cost-reduction capability of the novel contactor, the total direct air capture (DAC) cost could be reduced by approximately 30%.

During Phase II, Emissol plans to optimize their novel contactor for an even higher capture rate, as well as for greater DAC cost savings. The project team is working closely with a national lab on prototyping, testing, and manufacturing the contactor.

technical goals

- Reduce contactor thermal mass in order to minimize thermal energy and lower its associated costs (operating expenses [OPEX]).
- Study sorbent loading in mesopores of the contactor for enhanced, internal mass diffusion, further increasing CO_2 transport rate.
- Optimize the geometry of the contactor at unit level (e.g., to minimize pressure drop) and at system level (e.g., to meet the capture target at lowest cost).
- Develop a low-cost, scalable, cost-competitive manufacturing method to produce the novel honeycomb.
- Perform a techno-economic analysis (TEA) to assess the impact of the resulting contactor on reducing the total DAC cost.
- Develop a process model for parametric studies and data feeding into the TEA.

technical content

Honeycomb monolith substrates have found successful use in DAC. A noteworthy example is that by Global Thermostat (Figure 1), where such contactors coated with amine compounds adsorb CO_2, then desorb and release CO_2 every 15 minutes at near-perfect purity of 98–99%. Another example is Carbon Engineering Ltd., where a solvent could capture 1 million tonnes (Mt) of CO_2/year, used next to produce various products, such as synthetic fuels. The primary reason for Global Thermostat and Carbon Engineering using honeycomb-type contactors is that they provide plenty of surface area ideal for CO_2 adsorption/desorption while

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Monolith Amine-Based Sorbent for CO_2 Capture

participant:
Emissol LLC

project number:
SC0020860

predecessor projects:
N/A

NETL project manager:
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principal investigator:
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Emissol LLC
mansour.masoudi@emissol.com

partners:
Oak Ridge National Laboratory

start date:
06.29.2020

percent complete:
57%

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[1] National Academy of Science, Engineering and Medicine. "Negative Emissions Technologies and Reliable Sequestration: A Research Agenda." National Academies Press. (2019).

yielding very low pressure drop and, hence, low pumping power energy cost for air flow to pass through contactors.

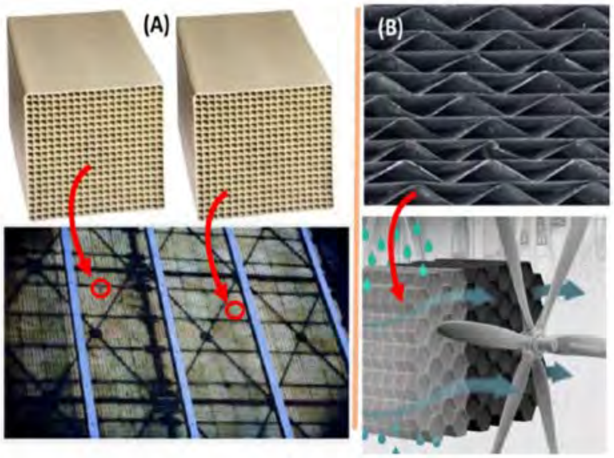

Figure 1: (A) Top: Ceramic honeycomb (monolithic) contactors used by Global Thermostat. Bottom: Their large stack at the Global Thermostat plant. (B) Top: Carbon Engineering's array of contactors, honeycomb-like structures (one section shown only) for air flow (bottom) and CO_2 removal using a solvent.

However, such honeycombs have one major limitation: in their straight channels, CO_2 species travel to the sorbent-coated wall (or to the solvent) via diffusion, an inherently slow process (i.e., the channel's base flow, the convection, has no role in CO_2 transport to the sorbent). Removing this major barrier, Emissol has invented a proprietary honeycomb contactor replacing the slow CO_2 diffusion with the much faster convective transport, hence dramatically increasing the rate of CO_2 transport to the sorbent (wall). Further, since the channel mass transfer increases faster than its friction force does, it yields a "net gain" in performance versus its pressure drop increase. The contactor makes available faster CO_2 adsorption/desorption rates (i.e., grams/seconds) and thus higher capture frequency. Therefore, the potential exists to replace mainstream contactors, some discussed above, with this project's transformational contactor, markedly reducing DAC cost. A block flow diagram of the overall DAC process is shown in Figure 2.

Particularly, Phase I results indicate that, given its markedly faster capture rate, the Emissol contactor can also be downsized by approximately 40% (relative to a typical, baseline contactors) without impacting the captured CO_2 target (tonnes/unit time), in turn enabling a major sorbent reduction by about the same ratio (40%). Since the adsorbent capital expenditure (CAPEX) forms more than 80% of the total DAC cost,[1] the savings yields a DAC cost reduction by approximately 30%—a marked reduction in the total DAC cost.

Phase II research and development (R&D) focuses on key tasks to further enhance the contactor impact on the total DAC cost reduction (i.e., above and beyond cost-saving gains achieved in Phase I).

Task 1. Reduce contactor thermal mass, to reduce thermal energy for desorption and its associated costs.

Task 2. Sorbent loading in mesopores of the contactor: sorbent-contactor optimization.

Task 3. Optimizing the contactor geometry, first at the honeycomb scale (local unit), and next at the system scale. Both efforts target maximizing cost savings for DAC.

Task 4. Developing a low-cost, scalable, manufacturing method.

Task 5. Develop a TEA.

Proposed Module Design – Honeycomb contactor with switching between adsorption and desorption modes.

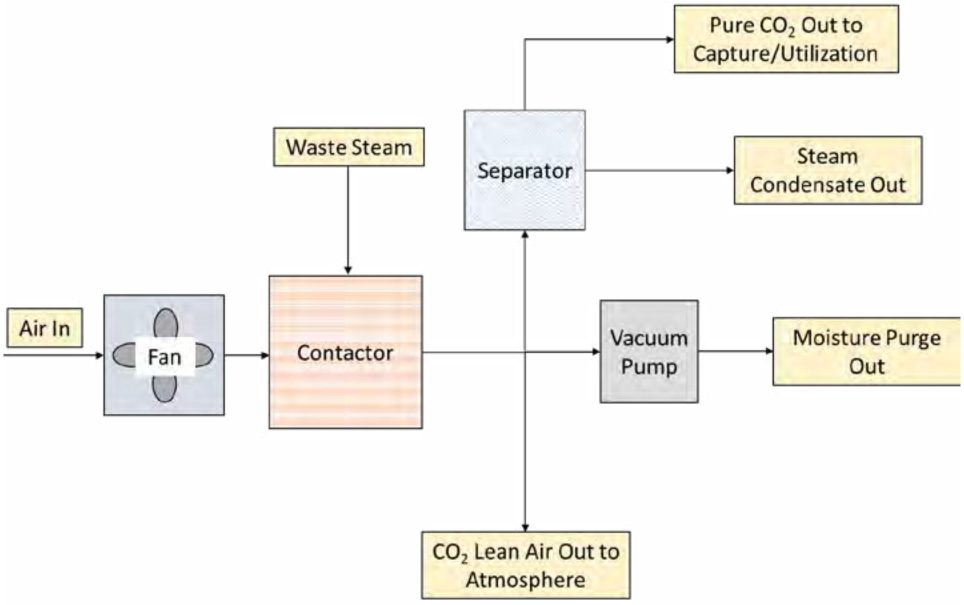

Figure 2: Block flow diagram of DAC system.

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The TEA calculation is based on the study referenced earlier via footnote.[1]

Scale of Validation of Technology Used in TEA – The TEA is based on contactor-scale modeling results. The model shows good agreement with the experiment.

technology advantages

- Novel contactor design.
- Reduced contactor size to roughly half the size of conventional honeycomb contactors.
- Reduced sorbent use (by approximately half).
- Enables faster capture cycles, hence accelerated capture/release cycle, and increases the net capture amount (tonne CO_2/day).
- Lowers thermal energy required for sorbent regeneration and low pressure drop.

R&D challenges

- Engineering-enhanced pore diffusion of CO_2 in the solid sorbent; managing the intricacy between support's pore size and powder (sorbent) pore size in a manufacturing process aiming at faster pore diffusion.
- Optimizing the contactor geometry at the honeycomb scale and at the system level.

status

Emissol has developed its own coating process for applying the sorbent to the structured support. The sorbent has been identified; honeycomb prototyping and model development and enhancements are currently under way.

available reports/technical papers/presentations

Masoudi, M. “Novel, Efficient, Low Cost Technology for Direct Air Capture of CO_2 and its Removal from Low Concentration Streams.” NETL Direct Air Capture Kickoff Meeting. February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Masoudi.pdf*.

MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent for DAC

participant:
Georgia Tech Research Corporation

project number:
FE0031952

predecessor projects:
N/A

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principal investigator:
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partners:
N/A

start date:
06.01.2019

percent complete:
83%

primary project goal

Georgia Tech Research Corporation is investigating the use of hybrid sorbents based on metal-organic framework (MOF, MIL-101(Cr)) materials functionalized with amine groups for the direct air capture (DAC) of carbon dioxide (CO_2) at sub-ambient conditions. The primary goal of the project is to tailor MIL-101(Cr)-based sorbents to overcome technical barriers associated with their application at sub-ambient temperatures/conditions and validate their amenability to practical DAC application. In this direction, the stability of the powder sorbents against adsorption-desorption cycles and oxidative degradation is being determined. MIL-101(Cr) MOFs are being studied alone and in the presence of amines that range in size from small molecules to oligomers. The synthesis and characterization of sorbent materials as powder, fiber, and monolith samples is being conducted. These materials are being tested for CO_2 adsorption performance with air feeds containing 400 parts per million (ppm) CO_2 at sub-ambient conditions above minus 20°C and below 25°C and varied humidity levels. Preliminary models of adsorption and desorption behavior are being developed and used to predict DAC process parameters. Furthermore, the possibility of the deployment of powder sorbents as practical structures for gas-solid contacting (i.e., monoliths and fibers) is being evaluated.

technical goals

- Development of powder MIL-101(Cr) amine sorbents and baseline testing.
- Systematic study of the influence of amine molecular weight on sorbent performance at sub-ambient conditions of varied humidity.
- Investigation of the incorporation of MIL-101(Cr) into fibers and monoliths.
- Computational studies to model adsorption and desorption equilibrium and kinetics of MIL-101(Cr)-amine material.
- Development of adsorption/desorption models used to predict DAC system parameters, including energy consumption, sorbent efficiency, and system size.
- Development of three-dimensional printing procedure for MIL-101(Cr) monoliths.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

Metal organic frameworks (MOFs) are two- or three-dimensional crystalline structures composed of metal nodes coordinated by organic linkers. These hybrid materials have demonstrated great potential for the capture of CO_2, with promising applications, either as CO_2 sorbents themselves or as supports for amine-based CO_2 capture. The use of MOFs, as compared to other commonly used supports (e.g., silica), provides a range of advantages, including:

i. High Brunauer–Emmett–Teller (BET) surface areas.
ii. Tunable pore characteristics.

iii. High pore volume.
iv. High density of open metal sites.
v. Stability under a wide range of conditions.

The last three features are highly desirable for functionalization of the support with amines. MIL-101(Cr) and $Mg_2(dobpdc)_2$ are two MOFs that offer potential to be a tunable platform for practical DAC. However, $Mg_2(dobpdc)$ has been reported to be unstable under humid conditions, and amine-ligated $Mg_2(dobpdc)$ has unsuitable sorption kinetics under DAC conditions. Contrary to this behavior, MIL-101(Cr) has been reported to possess good stability in boiling water, over a variety of pH conditions, and to exposure to sulfur dioxide (SO_2) and nitric oxide (NO). Thus, in this proposed work, the aim is to develop MIL-101(Cr)-based sorbents tailored for deployment under specific DAC conditions. MIL-101(Cr) is a three-dimensional framework with open chromium metal sites that, together with the open space within the porous framework, can provide “loading sites” for various amine species designed for CO_2 capture (Figure 1). The capabilities of this amine-functionalized MOF for CO_2 capture at varied CO_2 concentrations have been demonstrated, with reported CO_2 capacities under DAC conditions as high as 1.35 mmol/g (PEI-MIL-101(Cr)) and 2.8 mmol/g (TREN-MIL-101(Cr)). Although promising candidates as DAC sorbents, prior work evaluating the performance of these materials has focused on CO_2 adsorption at temperatures ranging from 25–100°C and studies of the effect of humidity have been minimal.

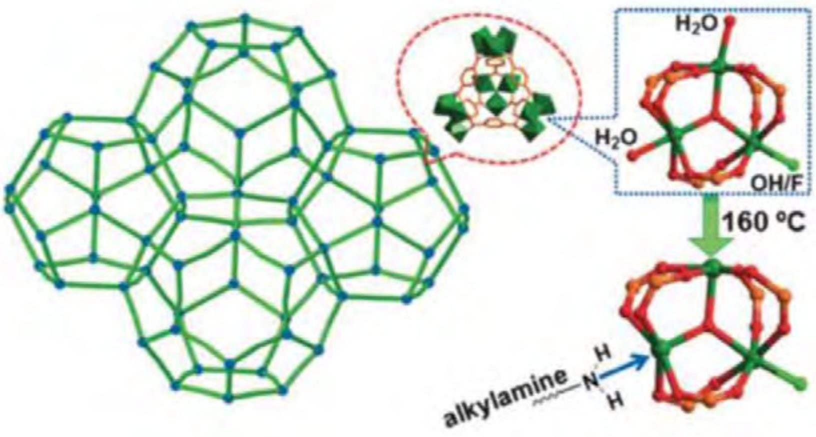

Figure 1: Schematic of amine functionalization of MIL-101(Cr).

The effective removal of carbon from the atmosphere by an air capture technology is known to depend on the specific climate (e.g., temperature and relative humidity [RH]) at a given location, so currently available data are only relevant to hot desert climates. If one considers the temperature spectrum for all the climate regions of the United States in 2019 (Figure 2), the variations in the temperature profiles are noticeable. Furthermore, sub-ambient temperatures (defined herein as temperatures below 20°C) are predominant among these regions for a large portion of the year. From a DAC deployment perspective, the diversity in the profiles reported in Figure 2 would lead to distinct temperatures for CO_2 capture at each of these locations. This would cause significant performance inconsistencies if an identical DAC technology were implemented across these locations. In the proposed work herein, the aim is to investigate the CO_2 adsorption capabilities of MIL-101(Cr)-amine sorbents focusing on this spectrum of overlooked temperatures (-20 to 20°C).

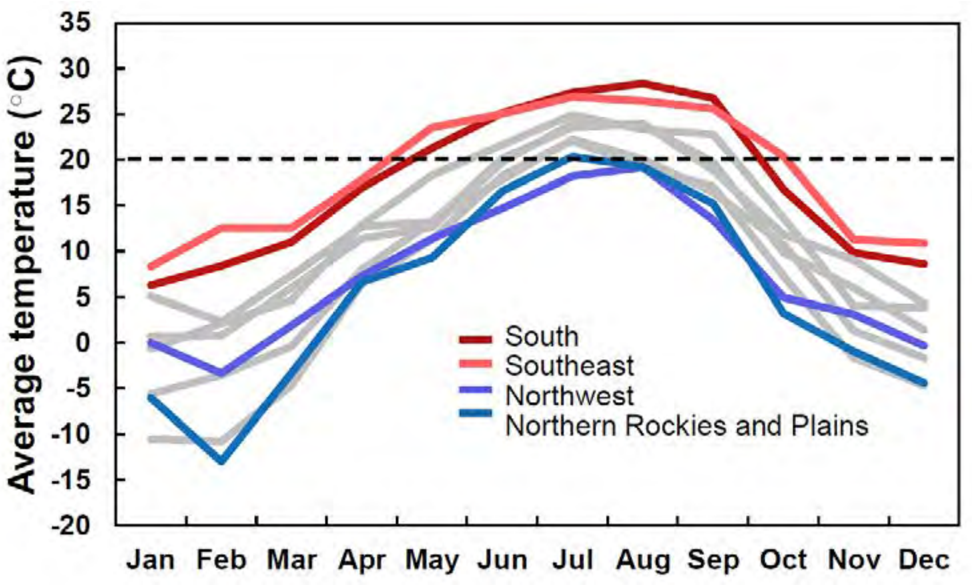

Figure 2: Summary of 2019 average monthly temperatures for U.S. climate regions. Data from the National Climatic Data Center. The gray lines include the following climate regions: Southwest, Ohio Valley, West, Northeast, Upper Midwest.

Separation Mechanism of MIL-101(Cr)/amine [FOA MRC1(b)]

The MIL-101(Cr)-amine hybrid materials follow the zwitterionic mechanism of CO_2 capture. This is the most common mechanism for solid adsorbents, where a zwitterion is formed via the interaction between CO_2 and an amine (process 1 in Figure 3). In the presence of a base, the zwitterion deprotonates to produce a carbamate (process 2 in Figure 3). In dry sorption conditions, a second amine species acts as the base, while in humid conditions, the water or hydroxide group may play this role. In humid conditions, one amine is able to capture up to one CO_2 molecule, improving the theoretical maximum CO_2/N ratio (i.e., amine efficiency) from 0.5 to 1. Under dry conditions, the placement of amines in close proximity (i.e., at high loading) is often used to achieve high amine efficiencies. For both sorption conditions (dry or humid), a sorbent that facilitates the access of CO_2 to the amine sites is required. In this direction, it is anticipated that for CO_2 capture under sub-ambient conditions, the decrease in temperature will increase the rigidity of polymeric amines, leading to high diffusional resistances and therefore compromising the reaction kinetics of CO_2 adsorption. To tackle this challenge, this project proposes a design of the MOF-amine hybrid sorbents where the effect of low molecular weight (LMW) aminopolymers on the CO_2 adsorption capacity and kinetics at sub-ambient conditions will be evaluated. Furthermore, the hypothesis is that the open Cr coordination sites in the MIL-101(Cr) will allow retention of LMW amines (e.g., TREN and tetraethylenepentamine [TEPA]), circumventing issues related to amine losses due to volatility. These losses will also be alleviated by the use of mild desorption temperatures (e.g., as low as 50°C). This approach introduces the idea of sorbent optimization based on DAC deployment location, where the use of LMW amine-based sorbents will be more favorable at ultra-low temperature, while the use of high molecular weight amine-based sorbents would be targeted for elevated temperature operation. The choice of MOF supports is crucial in this design as the absence of open metal coordination sites in silica, alumina, and related supports would preclude use of volatile LMW amines.

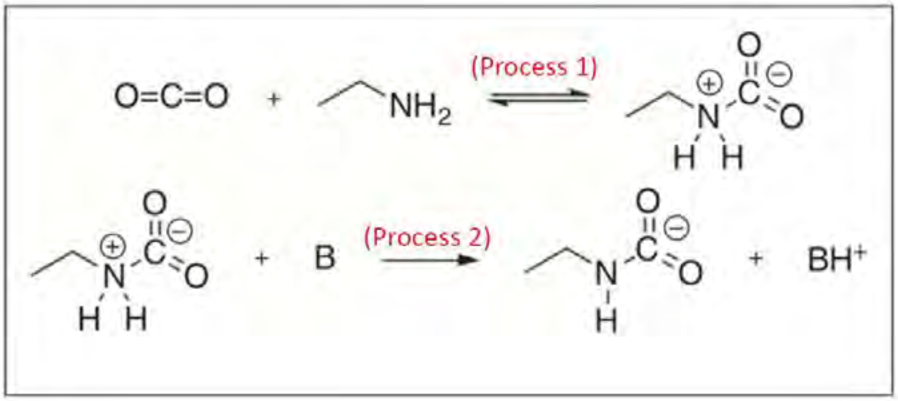

Figure 3: Mechanism of CO_2 capture involving (1) interaction between CO_2 and an amine followed by (2) deprotonation of resulting zwitterion in presence of a base.

Material Compatibility with DAC Conditions

The deployment of solid adsorbents for DAC applications offers a lower energy penalty during the adsorption-desorption process compared to aqueous sorbents, with the sorbents categorized as physisorbents or chemisorbents. At room temperature, physisorbent materials, such zeolite-based adsorbents, have shown appealing CO_2 capacities in pure CO_2 (~135 mg CO_2/g sorbent at 25°C in pure CO_2). However, given the physisorption nature of the uptake and consequential low selectivity between gases, these materials perform poorly at low CO_2 partial pressures, as demonstrated by the isotherms in Figure 4a. In this direction, chemical adsorption of CO_2 to the solid sorbent is more appropriate for DAC application, as it has been shown to be more efficient at extremely low CO_2 concentrations (ca. 400 ppm) (Figure 4a). Chemisorbents can be created by the functionalization of a solid support (e.g., silica, alumina or MOF) by amines. Moreover, functionalizing the support with amines that exhibit optimum adsorbate-adsorbent interaction strength, such as polyethyleneimine (PEI, -65 kJ/mol), provides near-ideal separation efficiency for DAC concentrations in temperature swing adsorption (TSA). In fact, in previous studies using MIL-101(Cr) as CO_2 sorbents at 25°C, it was demonstrated that the CO_2 adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines, such as PEI and TREN (Figure 4b).

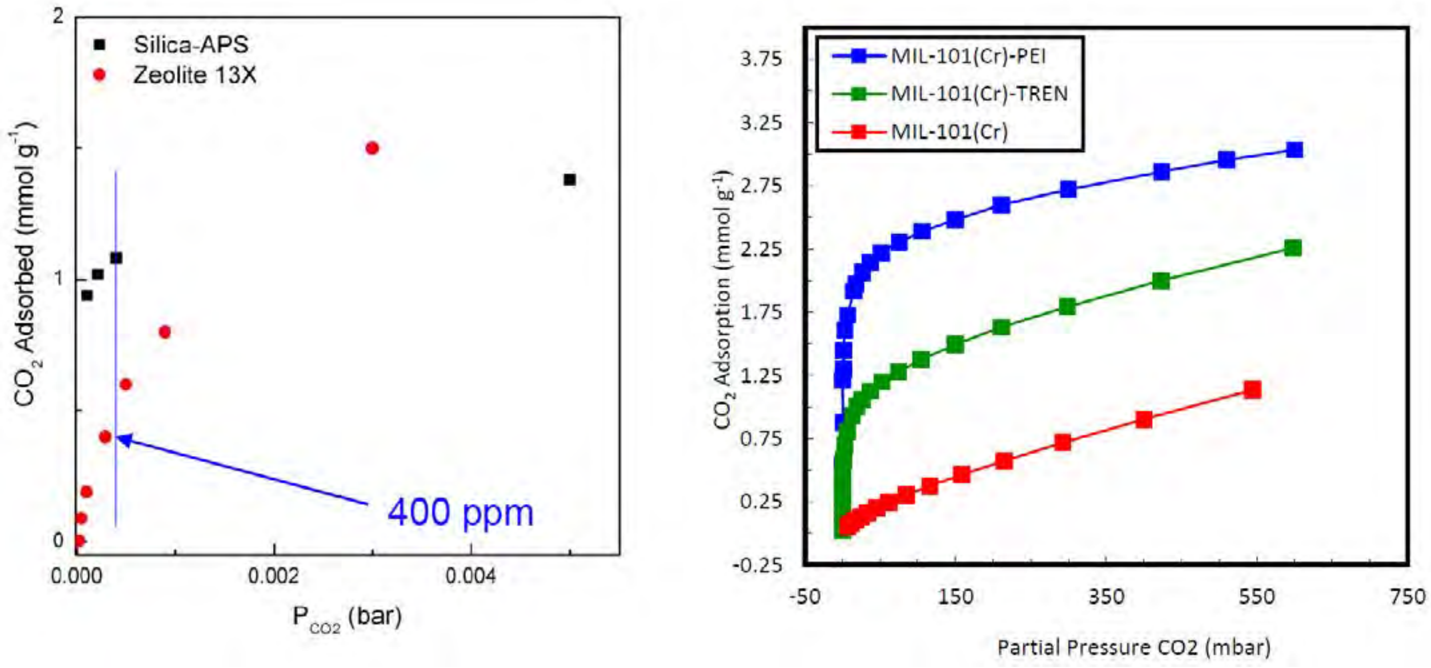

Figure 4: CO_2 adsorption as function of CO_2 partial pressure for: (a) physisorbent (zeolite) versus chemisorbent (silica-APS). (b) Bare MIL-101(Cr), MIL-101(Cr)-TREN (grafted), and MIL-101(Cr)-PEI.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	500 (estimated)	500
Bulk Density	kg/m^3	350 (measured)	350
Average Particle Diameter	mm	Crystal size: 1.5 – 8 x 10^{-4} Fiber diameter: 0.3 – 1.2 Monolith channel opening: 1 -6 (measured)	No change
Particle Void Fraction	m^3/m^3	Fibers: 0.35 (within fiber wall)	No change
Packing Density	m^2/m^3	Fibers: 5,000 – 10,000 (for bundle of fibers in shell and tube configuration)	No change
Solid Heat Capacity @ STP	kJ/kg-K	Crystals: 0.892 Fibers: 0.47 Monolith: 0.84	No change
Crush Strength	kg$_f$	N/A	N/A

Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	15	15
Adsorption			
Pressure	bar	0.0004 bar CO_2, 1 bar total	0.0004 bar CO_2, 1 bar total
Temperature	°C	-20 to 20°C	-20 to 20°C
Equilibrium Loading	g mol CO_2/kg	1.8 (PEI_MIL-101(Cr)) 2.1 (TEPA_MIL-101(Cr)) (Measured at 25°C)	1 – 4 (at -20°C)
Heat of Adsorption	kJ/mol CO_2	-90	-60
CO_2 Adsorption Kinetics	gmol/time	0.016 mmol/g/min (initial adsorption rate, measured at 25°C)	0.02 mmol/g/min (at -20°C)
Desorption (temperature swing adsorption)			
Pressure	bar	0.005 bar CO_2	0.1 – 1 bar CO_2
Temperature	°C	25 – 60°C	25 – 60°C
Equilibrium CO_2 Loading	g mol CO_2/kg	<0.2 (at 25 – 60°C)	<0.2 (at 25 – 60°C)
Heat of Desorption	- kJ/mol CO_2	40 - 95	60
CO_2 Desorption Kinetics	gmol/time	0.045 mmol/g/min (estimated)	0.1 mmol/g/min (at 25°C) 0.2 mol/g/min (at 60°C)

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	-4 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Amines in PEI or TEPA react with CO_2 to form ammonium carbamate under the dry condition and potentially also bicarbonate or carbonate in the presence of water

Sorbent Contaminant Resistance – In the targeted ambient air gas stream, oxygen and water can be the contaminants deteriorating the performance of the developed sorbent, However, the effect of the oxygen is assumed to be negligible due to the low operating temperature (from -20 °C to 25 °C). Under 70% relative humidity at - 20 °C, TEPA impregnated MIL-101(Cr) showed promising stability to humidity with ~0.8 mmol of CO_2/g of working capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Developed amine-MIL-101(Cr) materials were stable for 15 cycles of temperature swing adsorption and desorption process (from -20 to 25 °C or 60 °C) under dry conditions. Also, during 5 cycles of the breakthrough experiment at -20 °C 70% relative humidity with the same temperature swing process, TEPA impregnated MIL-101(Cr) showed stable working capacity with ~0.8 mmol of CO_2/g of sorbent

Flue Gas Pretreatment Requirements – Targeted air gas stream is directly from the ambient atmosphere

Sorbent Make-Up Requirements – MIL-101(Cr) synthesis requires chromium precursor and terephthalic acid as an organic linker. PEI and TEPA are used to functionalize MIL-101(Cr) for enhanced CO_2 capture performance. To incorporate MIL-101(Cr) into contactors such as fiber and monolith, cellulose acetate (CA) is used as a typical polymer matrix.

Waste Streams Generated – During the sorbent and contactor synthesis steps, chemical solvents such as methanol, hexane, N-methyl-2-pyrrolidone are generated as waste streams. In the CO_2 adsorption process, CO_2 depleted air, high purity CO_2, and water are generated.

Process Design Concept – Process flowsheet shown in Figure 5. Temperature vacuum swing adsorption using fiber or monolith contactor

Proposed Module Design – Fiber and monolith

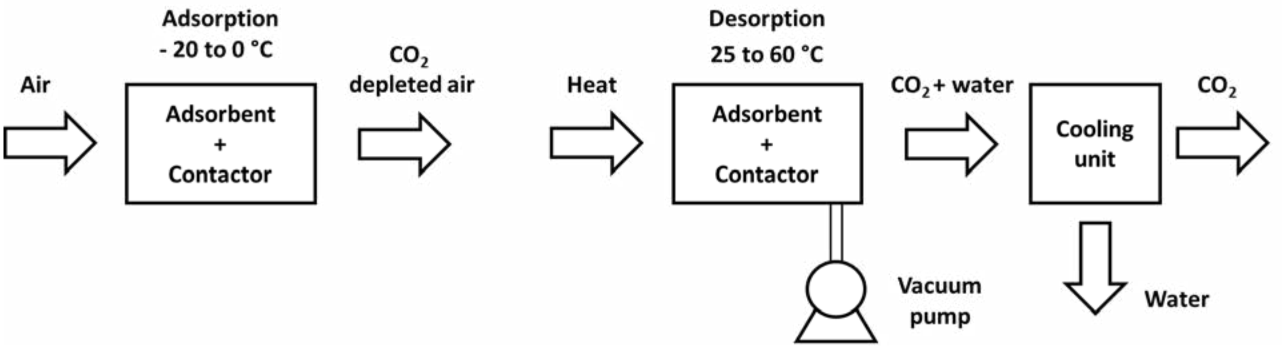

Figure 5: Process Flowsheet/block diagram.

Definitions:

The project is still ongoing and actual parameters from modules are required to estimate economic values.

Cost of Carbon Captured – Techno-economic analysis (TEA) is not a part of this project.

Cost of Carbon Avoided – TEA is not a part of this project.

Capital Expenditures – TEA is not a part of this project.

Operating Expenditures – TEA is not a part of this project.

Calculations Basis – Current R&D values for process parameters sometimes refer to estimates from the paper below, whereas sorbent performance parameters refer to new data generated in this project. Sinha, Anshuman, et al. "Systems design and economic analysis of direct air capture of CO_2 through temperature vacuum swing adsorption using MIL-101 (Cr)-PEI-800 and mmen-Mg_2 (dobpdc) MOF adsorbents." Industrial & Engineering Chemistry Research 56.3 (2017): 750-764.

Scale of Validation of Technology Used in TEA – A TEA is not being performed as part of the scope.

Qualifying Information or Assumptions:

1. Air is considered to have oxygen and nitrogen components in addition to the CO_2 (and 25% relative humidity) and the saturated steam is pure.
2. Ideal gas law and ideal mixtures are assumed for the non-condensable components. Temperature and concentration variations are neglected in the radial direction in the adsorbent film and monolith wall leading to a lumped model in the radial coordinate for these model elements.
3. Adsorbent film thickness is uniform in the axial direction.
4. During the desorption step, condensed water does not penetrate inside the MOF pores due to high flow rate of desorbed CO_2 from the MOF pores in the opposing direction. Thus, heat is conducted into the MOF and wall and is not transferred by diffusion of steam within the MOF phase following steam condensation.
5. Heat loss from the channel is negligible during all steps of the cycle.

technology advantages

- Chemical adsorption of CO_2 to the solid sorbent more efficient at extremely low CO_2 concentrations (ca. 400 ppm).
- Carbon dioxide adsorption performance of MIL-101(Cr) is greatly benefited by functionalization with amines.
- Carbon dioxide uptake at sub-ambient temperatures as low as -20°C enables operation in the temperature range of -20 to 20°C will cover a wide range of deployment locations.
- Regeneration of sorbent occurs at ambient 25°C.

R&D challenges

Carbon dioxide capture under sub-ambient conditions will increase the rigidity of polymeric amines, leading to high diffusional resistances and challenges in the reaction kinetics of CO_2 adsorption.

status

Georgia Tech Research Corporation completed preparation of MOF MIL-101(Cr) powder sorbents. The amine-impregnated MIL-101(Cr) powder show promising CO_2 uptake at -20°C due to enhanced physisorption at cold temperatures. The sorbents' sub-ambient capture capacity of 1.1 mmol/g at -20°C and low regeneration temperature of 25°C is believed to be a physisorption-dominant mechanism. The MIL-101(Cr)-based fiber sorbents were also manufactured and tested, showing 400 ppm CO_2 uptake of 1.2 mmol/g at -20°C. The MIL-101(Cr) was also successfully grown on the surface of cordierite monolith support. The sorbent loading on the monolith and CO_2 uptake optimization are currently being conducted, as is CO_2 adsorption isotherm modeling. Additional work is being conducted to ascertain which contactor is optimum for the DAC application, fiber versus monolith structures. Georgia Tech is continuing to collect CO_2 uptake isotherms, which will support the engineering process analysis for a larger-scale system.

available reports/technical papers/presentations

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Project Kickoff Meeting presentation, Pittsburgh, PA, December 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11047&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf*.

Ryan P. Lively, "MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions," Direct Air Capture Kickoff Meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-*

download.aspx?id=11046&filename=MIL-101(Cr)-Amine+Sorbents+Evaluation+Under+Realistic+Direct+Air+Capture+Conditions.pdf.

Christopher W. Jones, Ryan P. Lively, Matthew J. Realff, “MIL-101(Cr)-Amine Sorbents Evaluation Under Realistic Direct Air Capture Conditions,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Jones.pdf*

Guanhe Rim, Fanhe Kong, Mingyu Song, Cornelia Rosu, Pranjali Priyadarshini, Ryan P. Lively, and Christopher W. Jones,” Sub-Ambient Temperature Direct Air Capture of CO_2 using Amine-Impregnated MIL-101(Cr) Enables Ambient Temperature CO_2 Recovery,” JACS Au, 2022, accepted.

Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2

primary project goal

InnoSepra LLC is collaborating with Missouri University of Science and Technology, Arizona State University, and Adroitech Enterprise to evaluate transformational materials in structured forms for the direct capture of carbon dioxide (CO_2) from the air and to confirm a reduction in energy requirements compared to state-of-the-art technologies for direct air capture (DAC). The project activities include performing computational simulations, materials characterization, and lab-scale testing to optimize the performance of materials under DAC conditions, and developing a high-level process design to provide an estimate of electrical and thermal energy requirements, equipment sizing, and cost and carbon footprint. Finally, an assessment of the materials will also be made to evaluate the production of large-scale quantities for future commercial implementation.

technical goals

- Demonstrate the effectiveness of InnoSepra's DAC materials and technology for pipeline-quality CO2 with an energy consumption of less than 4 GJ/tonne.
- Demonstrate the potential of the transformational materials to reduce the energy required for DAC compared to current state-of-the-art technologies by up to 50%.
- Identify means to scale-up the materials to thousands of tonnes per year needed for commercial scale-up of DAC.

technical content

The technology utilizes physical sorbents in structured forms for capturing CO_2 directly from air. It leverages InnoSepra's past work on CO_2 capture from flue gas, as well as from low-concentration sources (1–1.5% CO_2), and adapts them to materials and processes developed for DAC. The use of structured sorbents minimizes the pressure drop associated with handling the very large volumes of air in DAC. While the driving force for DAC is significantly smaller due to a very low CO_2 partial pressure (about 0.04 kPa compared to a CO_2 partial pressure of about 15 kPa in the flue gas), the equipment size for the process per unit amount of CO_2 captured is minimized due to the use of high surface area sorbent materials and high CO_2 capacity of the materials under DAC conditions. Additionally, the materials have low heats of adsorption for CO_2 (40–45 kJ/mole) compared to amine-based sorbents (>100 kJ/mole) used for DAC. The combination of low-pressure drop, low heat of adsorption, very high surface-to-volume ratio for materials, and high CO_2 capacity at DAC conditions leads to a process with significantly lower energy requirements for DAC.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Structure Sorbents for DAC

participant:
InnoSepra LLC

project number:
FE0031953

predecessor projects:
N/A

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partners:
Missouri University of Science and Technology; Arizona State University; Adroitech Enterprise

start date:
10.01.2020

percent complete:
60%

The schematic in Figure 1 shows the DAC process. The pressure of ambient air is raised by 0.1–0.2 pounds per square inch (psi) in an induced draft (ID) fan and the compressed air is sent to a rotating bed moisture adsorption unit for removing moisture and a CO_2 adsorption unit in sequence. Because of the very large gas volumes involved with DAC, the system pressure drop for CO_2 capture needs to be minimized and structured sorbents are used in both stages for this to be accomplished. The pressure drop in each of these stages is expected to be less than 0.05 psi.

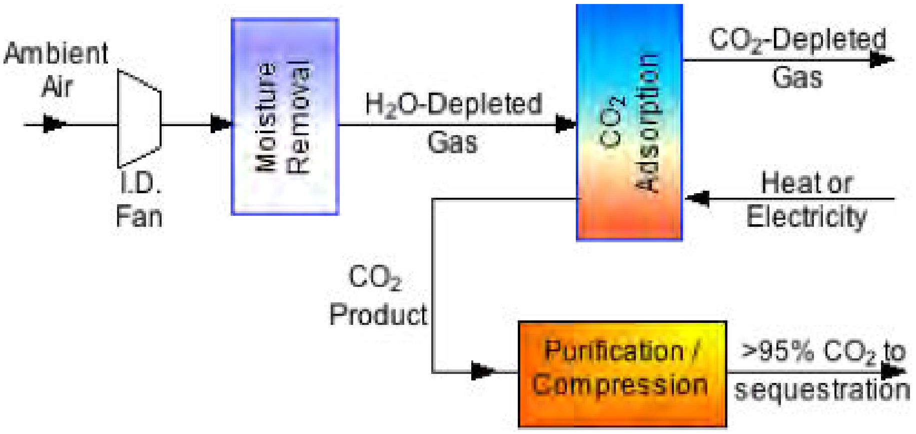

Figure 1: Process schematic for InnoSepra process.

The structured sorbents have significant advantages over particulate sorbents, including:

- Very low pressure drops (typically one-fifth to one-tenth of the particulate sorbents).
- Not subject to fluidization constraints or attrition issues.
- Very small effective particle size (less than 80 microns), leading to very short mass transfer zones.
- Ability to process significantly higher flows for a given bed volume.
- Can be fabricated with virtually any adsorbent, commercially available up to 10 feet in diameter.

A physical sorbent with high moisture capacity and very low CO_2 adsorption capacity is used during the dehumidification step. The rotating bed configuration for moisture removal is shown in Figure 2. Short bed depths coupled with a large open area (greater than 75%) lead to a very low pressure drop. One rotation of the wheel takes six–12 minutes, during which time the entire wheel undergoes adsorption (in the adsorption zone) and regeneration (in the regeneration zone). The drying process operates continuously. A rotating seal is used to separate the adsorption and regeneration zones. The moisture-depleted gas is sent to a CO_2 adsorber containing a sorbent that has a high CO_2 capacity at low CO_2 partial pressures.

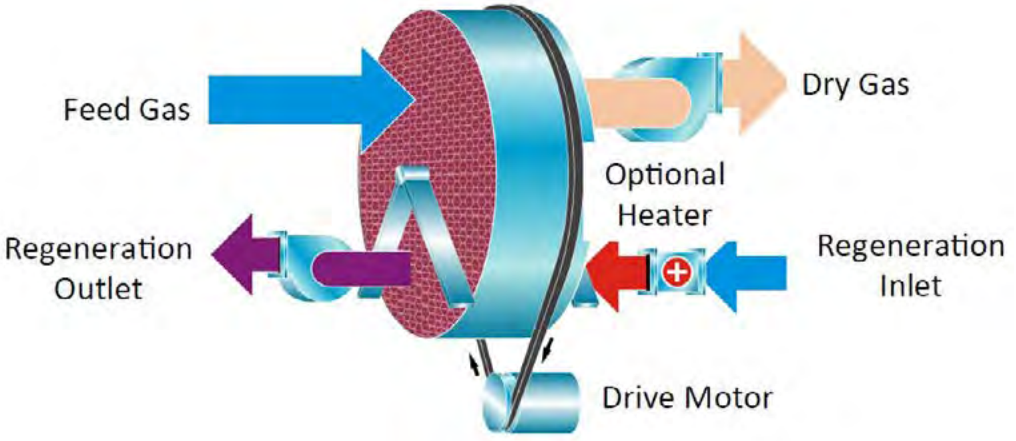

Figure 2: Rotating wheel dryer for feed dehumidification.

The CO_2 adsorber also contains structured sorbents. These sorbents can be thermally regenerated to produce a first CO_2 product stream that can be further purified and compressed to produce a CO_2 stream suitable for pipeline transport (Figure 1).

The breakthrough innovation is the use of a novel sorbent that leads to a significantly lower energy requirement for DAC compared to all known DAC technologies. It has a CO_2 capacity of more than 5 wt% at a CO_2 partial pressure of 400 parts per million (ppm) (0.04 kPa) and a temperature of 25°C. The heat of adsorption is approximately 44 kJ/mol of CO_2. The high CO_2 capacity and low heat of adsorption significantly reduce the regeneration energy needed for DAC. The sorbents are also very stable and exhibit no degradation in presence of any of the components in air.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,600	1,600
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	<0.1	<0.01
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1e+8	1e+8
Solid Heat Capacity @ STP	kJ/kg-K	1.00	1.00
Crush Strength	kg_f	>10	>10
Attrition Index	-	<0.01%	<0.01%
Thermal Conductivity	W/(m-K)	—	—
Manufacturing Cost for Sorbent	$/kg	15	10
Adsorption			
Pressure	bar	1.01	1.005
Temperature	°C	25-35	25-35
Equilibrium Loading	g mol CO_2/kg	0.9	1.2
Heat of Adsorption	kJ/mol CO_2	44	44
CO_2 Adsorption Kinetics	gmol/min	0.2	0.5
Desorption			
Pressure	bar	0.2-1.0	0.2-1.0
Temperature	°C	100-150	90-105
Equilibrium CO_2 Loading	g mol CO_2/kg	0.2	0.1
Heat of Desorption	kJ/mol CO_2	44	44
CO_2 Desorption Kinetics	gmol/min	0.4	0.6

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Physical

Sorbent Contaminant Resistance – No impact of oxygen and moisture in feed air, acid gas impurities are not relevant to DAC.

Sorbent Attrition and Thermal/Hydrothermal Stability – Very stable.

Sorbent Make-Up Requirements – At least five years life before any make-up is needed.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	N/A	N/A
Cost of Carbon Avoided	\$/tonne CO_2	N/A	N/A
Capital Expenditures	\$/tonne CO_2	N/A	N/A
Operating Expenditures	GJ/tonne CO_2	4.6	<4.0

Definitions:

Cost of Carbon Captured – The projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – The projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – No U.S. Department of Energy (DOE) reference case for DAC.

The Scale of Validation of Technology Used in TEA – Since this is a materials project, only power consumption numbers are provided in the techno-economic analysis (TEA).

technology advantages

- High CO_2 capacities at a CO_2 concentration of 400 ppm (greater than 4 wt%).
- Very long sorbent life (more than five years).
- Regenerable at low temperatures (less than 125°C).
- Can be quickly scaled-up to very large quantities for commercial-scale DAC.

- Potential for up to 50% reduction in the energy needed for DAC (less than 4 GJ/tonne).
- Potential for up to 50% reduction in the capture cost (less than $200/tonne).

R&D challenges

Fabrication of large quantities of structured sorbent and process demonstration at a commercially relevant scale.

status

InnoSepra Inc. has demonstrated CO_2 sorbent capacities between 3.5–4.5 wt% is possible from dilute source absorption 400-ppm CO_2 in the air at 25°C. Carbon dioxide breakthrough capacities between 2.5–3 wt% CO_2 have also been obtained. Modification of sorbents was also investigated to lower the amount of nitrogen co-adsorption while maintaining high CO_2 capacities. Fabrication, testing, identification, and downselection to two sorbent materials in structured form with a minimum 3.5 wt% CO_2 capacity was completed. Development of preliminary technical analysis was completed. This showed that sorbent material has at least 50% lower energy requirements for DAC when compared to the current state-of-the-art technologies.

available reports/technical papers/presentations

Ravi Jain, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/files/Transformational%20Sorbent%20Materials%20for%20a%20Substantial%20Reduction%20in%20the%20Energy%20Requirement%20for%20Direct%20Air%20Capture.pdf.*

Ravi Jain, Norberto Lemcoff, "Transformational Sorbent Materials for a Substantial Reduction in the Energy Requirement for Direct Air Capture of CO_2," Project kickoff meeting presentation, Pittsburgh, PA, September 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12367&filename=Transformational+Sorbent+Materials+for+a+Substantial+Reduction+in+the+Energy+Requirement+for+Direct+Air+Capture.pdf*.

Development of Advanced Solid Sorbents for Direct Air Capture

primary project goal

RTI International, partnered with Creare and Mohammed VI Polytechnic University, is developing two types of advanced adsorbent materials—metal-organic frameworks (MOFs) and phosphorous dendrimers (P-dendrimers)—for direct air capture (DAC) of carbon dioxide (CO_2). The sorbents are being synthesized, characterized, and optimized to achieve high CO_2 capacity at very low CO_2 partial pressures, high swing capacity, improved mass and heat transfer, and long operational life at low cost. The project team is testing two selected sorbents (one MOF adsorbent and one amine-P-dendrimer adsorbent) over 100 adsorption-desorption cycles in a laboratory-scale packed-bed reactor (PBR) and evaluating sorbent performance in the presence of contaminants (e.g., oxygen and water). The best performing sorbent will be evaluated for commercial production cost and scalability. Incorporation of the novel sorbents into a low pressure drop multichannel monolith-type reactor that can capture CO_2 from air at a cost of approximately $70/tonne of CO_2.

technical goals

- Develop MOF- and P-dendrimer-based sorbents for high durable DAC sorbent, to achieve high CO_2 capacity (in excess of 7–9 wt%) at low CO_2 partial pressures observed in air.
- Investigate the mass and heat transfer characteristics of select high CO_2 capacity solid sorbents when incorporated in a multichannel monolith-type reactor configuration.
- Develop computational fluid dynamics (CFD) model of the MOF and P-dendrimer sorbent to help understand the adsorber reactor design and optimize sorbent-absorber integration.
- Demonstrate long-term chemical and mechanical stability of select high CO_2 capacity sorbents (more than 100 cycles). The multicycle performance testing for both sorbents will be used for CFD model validation, including diffusion of gases into the porous sorbent materials.
- Evaluate the impact of sorbent contaminants present in air, such as oxygen (O_2) and water (H_2O), on these advanced solid sorbents at different temperatures and humidity levels.
- Perform a preliminary process design for DAC with a qualitative assessment of sorbent properties affecting the critical process design choices.
- Select sorbents that have high CO_2 capacity, have long-term stability, are low cost (less than $15/kg of sorbent), are contaminant resistant, and can be scaled rapidly in one to two years for future testing.

technical content

The RTI team is developing, studying, and comparing the performance of two novel materials, MOFs and P-dendrimers, for DAC that have the potential of significantly reducing the capital cost of the adsorbent while demonstrating high

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework and Phosphorous Dendrimer Sorbents

participant:
Research Triangle Institute

project number:
FE0031954

predecessor projects:
N/A

NETL project manager:
Mariah Richardson
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principal investigator:
Mustapha Soukri
Research Triangle Institute
msoukri@rti.org

partners:
Creare; Mohammed VI Polytechnic University

start date:
10.01.2020

percent complete:
80%

CO_2 working capacity at extremely low CO_2 concentrations (~400 parts per million [ppm]) and high CO_2 selectivity over moisture, oxygen, and nitrogen, which are major constituents of air.

RTI's MOF-Based Sorbent for DAC

RTI's MOF-based sorbent for DAC preliminary data NbOFFIVE-Ni ($[Ni(NbOF_5)(C_4H_4N_2)_2 \cdot 2H_2O]$) are very recently considered as ideal MOF materials for trace CO_2 capture. This MOF displayed square-like channels with contracted pore-aperture sizes ranging from 3.5–3.9 Å (Figure 1) and apparent specific Brunauer–Emmett–Teller (BET) surface area of around 250–300 m^2/g. As stated earlier, these fluorinated MOF platforms show very interesting carbon capture performances, explained by the combined synergetic effect of thermodynamics and kinetics associated with the small pore size of the 1-D channels aligned with a periodic array of fluorine moieties.

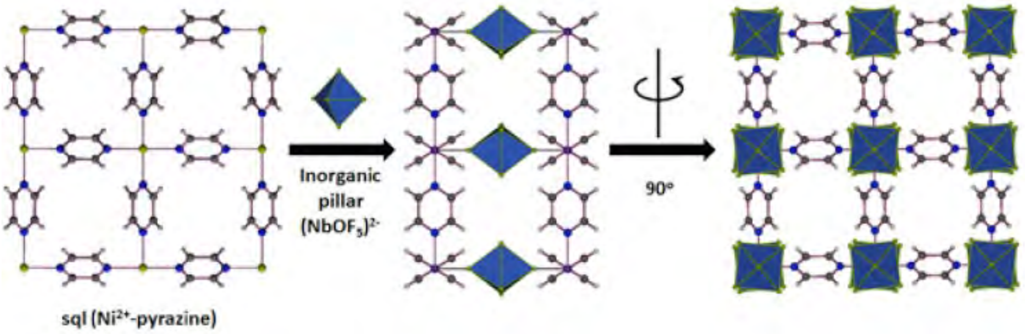

Figure 1: Structural representation of the NbOFFIVE-1-Ni (left), the 2-periodic square grid layer constructed by linking Ni(II) with pyrazine ligands, (middle), pillaring of square-grid layers by the (NbOF5)2- inorganic pillars, (right), square-shaped channels in the resultant 3-periodic pcu-MOF, NbOFFIVE-1-Ni.

RTI's partner Mohammed VI Polytechnic University has studied the CO_2 adsorption performance of NbOFFIVE-1-Ni at different conditions and has shown that this MOF exhibit 5.7 and 9.6 wt% at 400 ppm and 10 vol% CO_2, respectively (Figure 2), which surpasses the performance of the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. In addition, RTI has prepared and tested this MOF in thermogravimetric analysis (TGA) at 1,000 ppm CO_2 and in RTI's lab-scale PBR at 500 ppm CO_2. Fluorinated MOF, NbOFFIVE-1-Ni, exhibits the highest CO_2 gravimetric uptake (ca. 7.2 wt% at 1,000 ppm CO_2 and 6.5 wt% at 500 ppm CO_2) for a physical adsorbent at low partial pressures of CO_2.

The contracted square channels decorated with proximal fluorine moieties were believed to confer this MOF with the observed exceptional CO_2/nitrogen (N_2) selectivity. Moreover, NbOFFIVE-1-Ni presented an exceptional chemical stability especially toward water; hence, NbOFFIVE-1- Ni stands as the best physical adsorbent material for CO_2 capture from atmospheric air with a CO_2 gravimetric uptake (at 400 ppm), 300% higher than the reference physical adsorbent, namely SAPO- 34(Sr^{2+}). The RTI team will further evaluate the performance of NbOFFIVE-1-Ni as an advanced sorbent for DAC, in particular, the long-term cycling and the effect of contaminants.

The competition of CO_2 adsorption with water vapor is a significant challenge for physisorbent materials in CO_2 capture, either from DAC or from flue gas. However, fluorinated MOFs with high uniform charge density and small pore sizes such as MFFIVE-1-Ni will enhance the affinity of MOFs for water molecules in the highly confined pore system without affecting CO_2 adsorption. For example, these characteristics permitted water and CO_2 to adsorb at distinct sites. In particular, water will preferentially adsorb to the open metal coordination sites, and CO_2 will preferentially adsorb via interactions with the fluorine moieties.

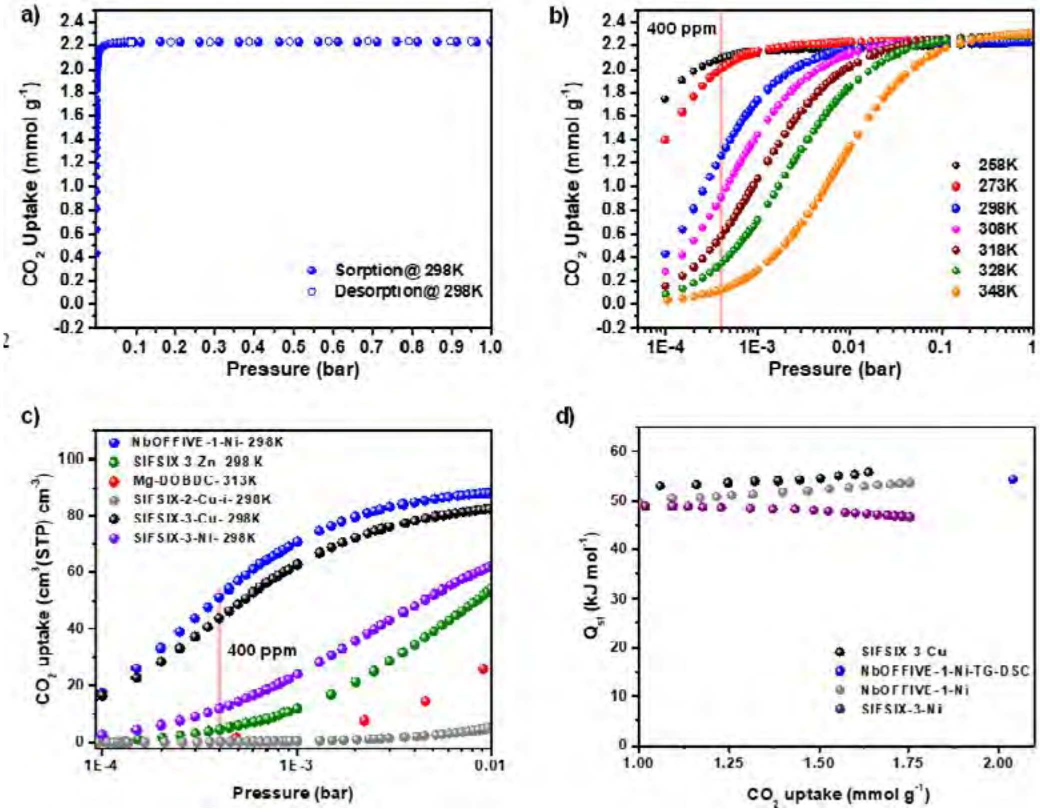

Figure 2: (a) CO_2 adsorption isotherm for NbOFFIVE-1-Ni up to 1 bar and 298 K. (b) CO_2 adsorption isotherms for NbOFFIVE-1-Ni at different temperatures. (c) Comparison of the CO_2 uptake at low pressures between the NbOFFIVE-1-Ni and the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. (d) CO_2 heat of adsorption for NbOFFIVE-1-Ni as compared to SIFSIX-3-Ni and SIFSIX-3-Cu, determined using multiple CO_2 adsorption isotherms and TG-DSC measurements.

RTI's P-Dendrimer-Based Sorbent for DAC

Under a U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL)-funded project (DE-FE0026432), RTI developed a novel water stable solid sorbent that was produced in 91% yield by crosslinking polyethyleneimines (PEIs) with polyaldehyde P-dendrimers (Figure 3), capturing on average 13.1 wt% CO_2 from simulated flue gas over 350 cycles (700 continuous hours running with no degradation or loss of CO_2 observed). The sorbent shows excellent thermal and chemical stabilities when operating under simulated flue-gas conditions with rapid kinetics for both adsorption and regeneration. This sorbent was also tested, after two years stored in the bench at 25°C, for CO_2 capture at 500 ppm of CO_2 in RTI's PBR. For the adsorption condition, the sorbent was exposed to 150 standard cubic centimeter (sccm) of 500 ppm-CO_2 in air at 25°C in the presence of 40% relative humidity (RH). The sorbent regeneration was performed by heating the sorbent to 80°C with 40% RH while monitoring the CO_2 desorbed from the sorbent at the reactor outlet. The CO_2 loading was determined from both the adsorption and regeneration steps for comparison. This adsorbent has demonstrated a CO_2 capacity of 7.45 wt% with 100% regeneration (80°C) and no degradation or capacity loss over eight cycles.

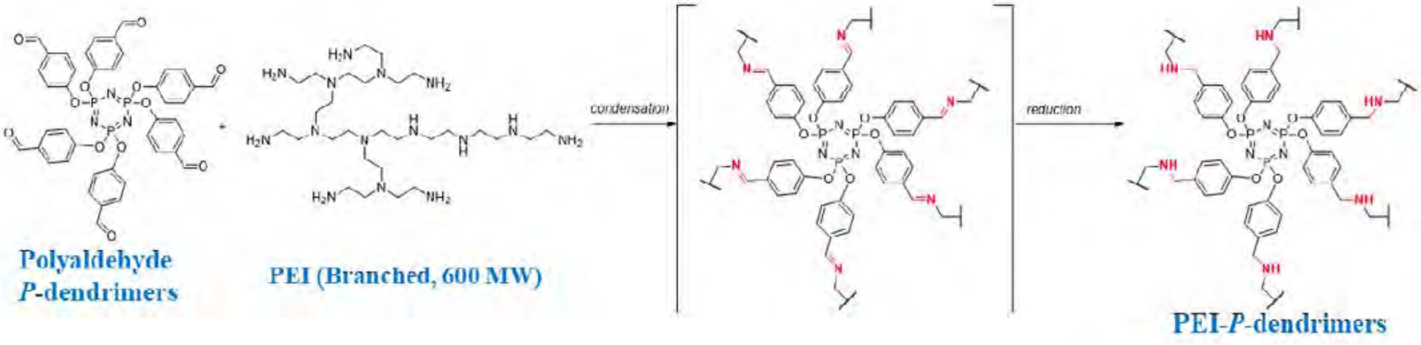

Figure 1: Synthesis of PEI-P-dendrimer.

The RTI team will prepare new sorbents with different textural properties and functionalized by grafting three polyamines: short chain ethylenediamine, 600 MW PEI, and 10,000 MW PEI and a polyaldehyde P-dendrimer crosslinker. To improve the capacity of the sorbent for DAC, RTI will optimize the material's pore size, pore volume, and surface area through a neutral templating cycle route and disrupt the hydrogen bonding between dendrimers for improved CO_2 uptake.

technology advantages

- High-capacity, fast kinetics, robust cycling, facile/cheap synthesis procedures, and easy scalability.
- Low-cost sorbents.
- Selective binding for CO_2.
- Ultra-microporous fluorinated MOFs offer fast sorption kinetics to enable selective capture of CO_2 over both N_2 and H_2O (low % RH), effective for trace CO_2 capture under both dry and humid conditions.
- The P-dendrimer amine-based sorbents perform very well under DAC conditions regardless of concentration of water vapor in air.

R&D challenges

- Improve performance under the presence of contaminants.
- Demonstrate the scale-up of selected candidate sorbents.

status

MOF synthesis and characterization of three different MOFs were accomplished in collaboration with Mohammed VI Polytechnic University. The CO_2 capture and kinetics under optimal conditions were determined and one MOF was evaluated using TGA and PBR for CO_2 capture uptake under relevant DAC conditions. The P-dendrimer amine sorbents were prepared using different amines ranging from short (ethylene diamine) to branched (polyethyleneimine) and tested in the PBR to determine their CO_2 capture uptake under the optimal conditions. The best performing amine sorbent is currently being evaluated for chemical stability under multi-cycle performance and under different RH. Long-term multi-cycle testing, air-gas contaminant evaluation, and sorbent scale-up and cost evaluation are currently being conducted.

available reports/technical papers/presentations

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11053&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11052&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Soukri.pdf*

AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere

primary project goal

General Electric Research (GE) has partnered with the University of California, Berkeley (UCB) to develop an advanced integrated reticular sorbent-coated system to capture carbon dioxide (CO_2) from the atmosphere ("AIR2CO2"). The system integrates pioneering metal-organic framework (MOF) sorbents and sorbent-binder composite coatings to capture and release atmospheric CO_2. UCB is building on their benchmark MOF sorbent to synthesize, test, downselect, and sufficiently scale a next-generation sorbent with optimized overall CO_2 adsorption capacity and thermal and chemical stability. GE is developing a robust MOF sorbent-binder formulation and coating process and integrating the advanced sorbent into an additively manufactured substrate. Component and system modeling of the AIR2CO2 process is being performed based on laboratory-scale experimental results and used to develop a techno-economic model that will inform future development of the sorbent material and AIR2CO2 contactor.

technical goals

- Integrate UCB's CO_2-capture MOF sorbents and GE's sorbent-binder coating technology into a viable AIR2CO2 material system.
- Build on benchmark MOF-808-Gly to synthesize, test, downselect, and sufficiently scale a next-generation sorbent.
- Conduct AIR2CO2 lab-scale component and process modeling, including mass-energy balancing and techno-economic modeling.
- Develop a robust MOF sorbent-binder formulation and coating process and integrate the advanced sorbent into an additively manufactured substrate.

technical content

The National Academies of Sciences, Engineering, and Medicine established that commercial viability of sorbent-based direct air capture (DAC) technologies requires the development of sorbents with higher capacities and faster reaction kinetics, as well as process intensification, including more effective mass and thermal transport and a lower pressure drop in the contactor. To address these challenges,GE and UCB propose to develop:

1) Advanced sorbents that build on UCB's promising benchmark Technology Readiness Level 2 (TRL 2) MOF sorbents.
2) A robust MOF-binder composite that yields greater than 90% enriched CO_2 directly from the atmosphere.
3) A conceptual design based on sorbent material and system modeling for an AIR2CO2 contactor that integrates the advanced sorbent with a high surface area, additively manufactured heat exchanger.

The AIR2CO2 contactor vision capitalizes on the unique capabilities of additive manufacturing to enable the fabrication of and sorbent integration into structures

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework-Based Sorbent for DAC

participant:
General Electric Research

project number:
FE0031956

predecessor projects:
N/A

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David Moore
General Electric Research
moored@research.ge.com

partners:
University of California, Berkeley

start date:
10.01.2020

percent complete:
83%

with larger surface area/weight ratios and lower pressure drops than conventional "honeycomb" designs. The robust coating of a thin sorbent layer on the structured walls is critical to realize an advanced AIR2CO2 contactor (Figure 1). Figure 1a conceptualizes the AIR2CO2 system, which undergoes alternating adsorption/desorption cycles for continuous CO_2 removal from air.

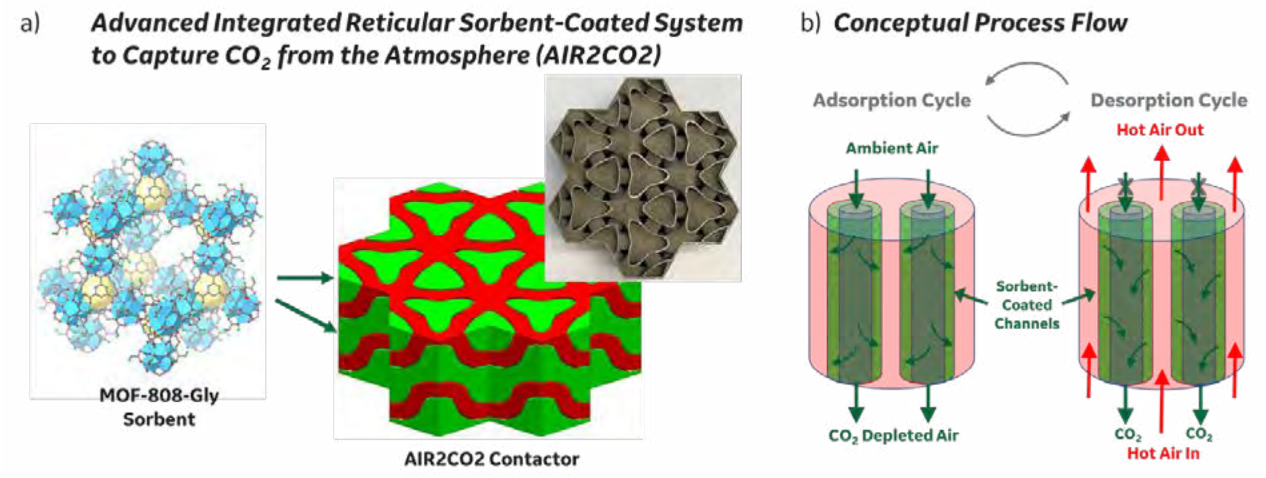

Figure 1: (a) Sorbent-coated contactor design showing sorbent-integrated channels (green) and hot air channels for desorption (red). (b) Conceptual process flow within alternating adsorption/desorption cycles.

Figure 1b shows a process flow rendering of the AIR2CO2 contactor design. The first contactor undergoes an adsorption cycle as ambient air flows through it, while the second contactor experiences a high-temperature (110°C) desorption cycle to release CO_2 and regenerate the sorbent. When the sorbent in the first contactor approaches its full adsorbent capacity, the air flow through the contactor is shut down and directed to the second contactor. MOFs, a class of porous, crystalline materials composed of metal ions joined by organic linkers, are the materials enabler for the AIR2CO2 material system. MOF sorbents demonstrate promising CO_2 sorption capacities and, more importantly, have the potential for significantly better performance than the current state of the art. MOF-808-Gly has been identified as a benchmark sorbent for CO_2 adsorption under DAC conditions. Figure 2a shows MOF-808-Gly and the CO_2 binding site consisting of five glycinate ligands coordinated to the $Zr_6O_4(OH)_4$ secondary building units in a bidentate fashion, which results in an amine loading of 3.3 mol/kg MOF. These amine groups enable chemisorption of CO_2 to occur at low partial pressures and in the presence of water, as evidenced by the dry (black) and humid (red) CO_2 adsorption isotherms (Figure 2b). Carbon dioxide reacts with the pendant amine groups to form bicarbonate (top), carbamate (middle), or carbamic acid (bottom), depending on the water content of the airstream examined. Covalent attachment of amine groups to the organic linker, rather than ionic attachment at a hydrolytically unstable metal site, allows for increased amine density (i.e., increased CO_2 capacity) and increased framework stability. Additionally, control of amine nucleophilicity and steric properties will reduce the heat of desorption of CO_2, facilitating faster CO_2 desorption kinetics and reducing the energy required to desorb CO_2.

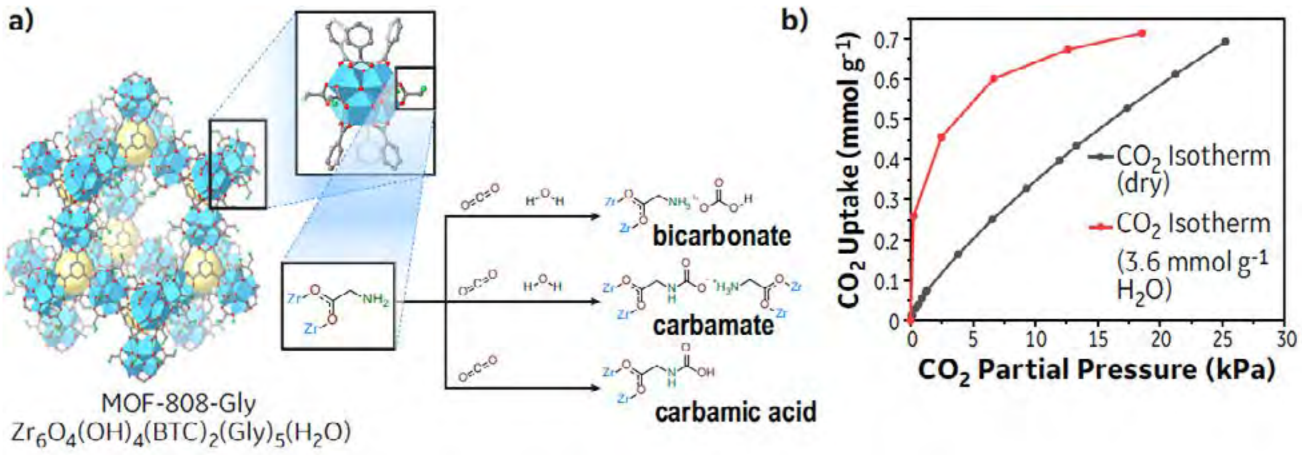

Figure 2: MOF-808-Gly benchmark MOF: (a) molecular structure and CO_2 adsorption mechanisms and (b) dry and humid CO_2 isotherms.

The two key innovations of the AIR2CO2 program include advanced sorbent architectures with high capacity and rapid sorption kinetics, and a sorbent-binder slurry and coating process that enables integration into an additively manufactured contactor that will ultimately reduce equipment size and pressure drop.

The currently available benchmark MOF-808-Gly (Figure 2) was designed for and performs well for post-combustion CO_2 capture, in which physisorption of CO_2 is responsible for the majority of the CO_2 captured. At low CO_2 concentrations, physisorption of CO_2 has a lower driving force, and chemisorption is the predominant capture mechanism. MOF-808-Gly exhibits low CO_2 capacity because of poor utilization of the amine groups required for chemisorption of CO_2, which translates to a higher thermal cycling energy penalty. Consequently, a large potential to improve CO_2 capacity of the benchmark MOF at DAC conditions exists. MOF capacity will be improved by increasing utilization of amine groups, accomplished by more efficient amine deprotonation during post-synthetic activation. Further enhancements will be achieved by increasing the density of amine groups loaded into the sorbent framework and by decreasing the heat of CO_2 desorption through incorporation of secondary amines into the structure. Integration of next-generation MOF sorbents into the AIR2CO2 contactor will result in an additional 40% lower energy consumption as a result of lower pressure drop across the contactor. Overall energy requirements for the AIR2CO2 concept are projected to be 60–70% lower than amine-functionalized zeolites. Moreover, initial projections show next-generation MOFs have greater than 40% lower energy requirements than aqueous amines for post-combustion CO_2 capture.

The advanced MOFs and sorbent-binder coating process that will be developed in the project have the potential to dramatically reduce DAC costs to \$20–80/ton CO_2. This conclusion incorporates the assessment by the National Academies of Sciences, Engineering, and Medicine of DAC CO_2 capture costs using sorbent technologies. The study evaluated sorbent and contactor performance for a generic sorbent across a range of parameters and assumptions, and concluded that CO_2 costs were \$18–\$1,076/ton CO_2. Furthermore, successful completion of this project will be a groundbreaking step in decarbonization efforts, as the technology will also be competitive with post-combustion CO_2 capture costs.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	950	950
Bulk Density	kg/m^3	450	450
Average Particle Diameter	mm	0.002-0.01	0.005
Particle Void Fraction	m^3/m^3	0.3	0.3
Packing Density	m^2/m^3	~7.4×10^5	~5.6×10^5
Solid Heat Capacity @ STP	kJ/kg-K	0.7	0.7
Crush Strength	kg_f	Not determined	Not determined
Attrition Index	-	Not determined	Not determined
Thermal Conductivity	W/(m-K)	Not determined	Not determined
Manufacturing Cost for Sorbent	\$/kg	—	<10
Adsorption			
Pressure	bar	0.0004	0.0004
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.34	2.3
Heat of Adsorption	kJ/mol CO_2	~72	72
CO_2 Adsorption Kinetics	gmol/g·min	~0.14 (meas. at 15% CO_2)	0.2
Desorption			
Pressure	bar	<0.0004	<0.0004
Temperature	°C	90-120	80-110
Equilibrium CO_2 Loading	g mol CO_2/kg	~0.03	0.25
Heat of Desorption	kJ/mol CO_2	~72	72
CO_2 Desorption Kinetics	gmol/g·min	~0.13 (meas. at 15% CO_2)	0.2
Proposed Module Design			*(for equipment developers)*
Flow Arrangement/Operation	—	—	

Flue Gas Flowrate	kg/hr		—	
Space Velocity	hr^{-1}		150,000	
Volumetric Productivity	gmol CO_2/(hr $l_{absorber\ bed}$)		2	
CO_2 Recovery, Purity, and Pressure	% / % / bar	—	—	—
Adsorber Pressure Drop	bar		0.0015	
Degradation	% capacity fade/cycle		0.0001	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

***Atmospheric Air Feed-Gas Assumptions*:**

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_X**	**NO_X**
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – At high CO_2 partial pressures both chemisorption and physisorption of CO_2 occurs. At DAC conditions (0.04 kPa CO_2) only chemisorption of CO_2 occurs as described in Figure 2 and accompanying text.

Sorbent Contaminant Resistance – Nitrogen oxide (NO_X) is not expected to have a significant impact on sorbent performance; however, reaction of amine-based sorbents with sulfur oxide (SO_X) to form heat stable salts is a known issue that will slowly decrease sorbent capacity.

Sorbent Attrition and Thermal/Hydrothermal Stability – Attrition is not anticipated to be a concern because the sorbent is integrated into a polymeric coating on the surface of the heat exchanger. Long-term thermal/hydrothermal stability of the sorbent-binder composite under operating conditions is unknown; however, the sorbent has been cycled approximately 80 times with no detectable decrease in CO_2 capacity.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	185	88
Cost of Carbon Avoided	\$/tonne CO_2	NA—	NA—
Capital Expenditures	\$/tonne CO_2	50	48.3
Operating Expenditures	\$/tonne CO_2	100	39.7

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – The calculation basis for the TEA was from "Quality Guidelines for Energy System Studies: Performing a Techno-Economic Analysis for Power Generation Plants," National Energy Technology Laboratory, DOE/NETL-2015/1726, July 2015. The approach follows the guidelines for the aspirational performance of a new technology.

Scale of Validation of Technology Used in TEA – The numbers in the TEA were validated using the scaled model.

technology advantages

- Two contactors operate in alternating adsorption and desorption modes to continuously remove CO_2 from air.
- High amine loading of MOFs (3.3 gmol/kg).
- High thermal stability inherent to MOFs.
- MOFs can be designed to exhibit high hydrolytic stability.
- High CO_2 capacity, fast sorption kinetics, and novel contactor designs would reduce energy requirements by 60–70% versus state-of-the-art DAC systems (liquid solvent and solid sorbents).

R&D challenges

- Evaluation of new MOF-binder composite coatings, cyclability, thermal stability.
- Post-AIR2CO2: Bench-scale testing of coated additively printed parts; techno-economics; 1 kg CO_2/day demo.
- Scale-up potential: demonstration scale with full-size additive contactor.

status

The AIR2CO2 lab-scale test apparatus has been designed and assembled at GE for evaluation of MOF-binder composite formulations under DAC-relevant conditions. The 1-kg benchmark MOF was successfully scaled. Next-generation, high-capacity sorbent is under development. The AIR2CO2 lab-scale test apparatus has been commissioned for operation. The contactor coating formulation and process development is ongoing. The leading MOF-binder composite formulations exhibit only approximately 20% decrease in sorption capacity versus the powdered sorbent. This is consistent with projected performance of the envisioned AIRCO2 contactor relative to the powdered MOF.

available reports/technical papers/presentations

David Moore, "AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-*

download.aspx?id=11061&filename=AIR2CO2%3a+Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+CO2+from+the+Atmosphere.pdf.

David Moore, “AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere,” Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11060&filename=AIR2CO2%3a+Advanced+Integrated+Reticular+Sorbent-Coated+System+to+Capture+CO2+from+the+Atmosphere.pdf*.

David Moore, Omar Yaghi, “AIR2CO2: Advanced Integrated Reticular Sorbent-Coated System to Capture CO_2 from the Atmosphere,” 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Moore.pdf*

Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2

primary project goal

Susteon Inc., in partnership with the University of Wyoming (UWy), is working to develop solid sorbent materials that have much higher working carbon dioxide (CO_2) capacity and can be regenerated at lower temperatures than current state-of-the-art materials. Structured sorbent beds can be constructed using these sorbents for low pressure drop operation to achieve reduced costs for direct air capture (DAC) of CO_2. The project aims to develop amine-doped solid sorbents catalyzed by a novel ionic liquid (IL) that have the potential to increase the CO_2 adsorption and desorption rate by several orders of magnitude as compared with non-catalyzed sorbents.

technical goals

- Develop amine-doped solid sorbents catalyzed by an IL that have the potential to increase the CO_2 desorption rate by several orders of magnitude at desorption temperatures of approximately 80°C.
- Evaluate the catalyzed amine-based sorbents to determine CO_2 desorption and adsorption kinetics.
- Based on the experimental results, develop a conceptual process design for the sorbents applied in a DAC system and conduct a preliminary cost analysis to assess the potential of the novel sorbent to reduce the cost of DAC.

technical content

Sorbents for DAC application must have several characteristics: (i) high selectivity for CO_2 adsorption over the other components present in the air (such as nitrogen [N_2] and oxygen [O_2]), (ii) high CO_2 working (adsorption) capacity, (iii) mild conditions for regeneration (usually induced by pressure or temperature swings), (iv) high stability and resistance against impurities and moisture, and (v) fast CO_2 adsorption and desorption kinetics. Amine-doped solid sorbents have been proven effective for DAC and can be regenerated by heat or by a combination of heat and steam. Lowering the regeneration temperature, and hence opening a way to use waste heat for sorbent regeneration, can significantly lower the cost of DAC. The IL catalysts can be easily added to amine-doped solid sorbents because the IL is not volatile and can be easily mixed with possible amine molecules such as polyethyleneimine (PEI), polypropyleneimine (PPI), etc. Furthermore, their catalytic effect has been studied extensively at UWy and proven effective when added in parts per million (ppm) concentrations in a monoethanolamine (MEA) solution. The IL has also been added to commercial amine-doped silica sorbents and tests have shown that the IL is effective in catalyzing solid sorbents for DAC applications with increased CO_2 working capacity, as well as adsorption and desorption kinetics. This combination of industrially utilized amine-based sorbents with a proven catalyst to form a new class of materials for DAC provides a technically viable pathway for reducing the cost of DAC to less than $100/tonne of CO_2.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine-Doped Sorbent Catalyzed by Ionic Liquid for Direct Air Capture of CO_2

participant:
Susteon Inc.

project number:
FE0031965

predecessor projects:
N/A

NETL project manager:
Carl Laird
carl.laird@netl.doe.gov

principal investigator:
James Zhou
Susteon Inc.
sjz@susteon.com

partners:
University of Wyoming

start date:
10.01.2020

percent complete:
82%

ILs, consisting of organic cations and organic or inorganic anions, are environmentally friendly due to their various desired characteristics, including high chemical/thermal stability, tunable physicochemical characters (acid/base sites), low corrosiveness, and low heat capacity, which is highly desirable for CO_2 capture systems. This project is aimed at utilizing the catalytic activity of a novel IL for DAC application by improving CO_2 adsorption and desorption kinetics. A new bifunctional IL has been discovered with the functionality for high catalytic activity in CO_2 capture solvents and sorbents due to the presence of Brønsted acid sites. This IL has been successfully used for significant acceleration of chemical reactions between amines and CO_2. It has also been utilized in modifying other catalysts for improving their catalytic performance. Nevertheless, it has never been used for enhancing the performance of solid CO_2 capture agents prior to this work, but has shown promising results with liquid amines (discussed later in this technology sheet). This project is focused on integrating this IL catalyst into amine-doped solid sorbents to develop a new generation of CO_2 capture sorbents with significantly higher adsorption and desorption rates and lower desorption temperatures (~80°C).

Previous tests were carried out to measure CO_2 absorption and desorption performance with 20 wt% MEA solution catalyzed by the IL catalyst. The absorption process was carried out with 100 grams of absorbent solution with s gas flow rate of 500 mL/min. The gas was composed of 80 vol% N_2, 10 vol% CO_2, and 10 vol% O_2, which is similar to a typical flue gas composition from a coal-fired power plant, except for the higher O_2 content. The absorption process was carried out until 13 minutes. The optimal IL dosage was found to be about 2,000 parts per million weight (ppmw) for this case. As shown in Figure 1, the IL catalyzed both CO_2 absorption and desorption processes (green is without the IL addition) and (orange is with IL addition).

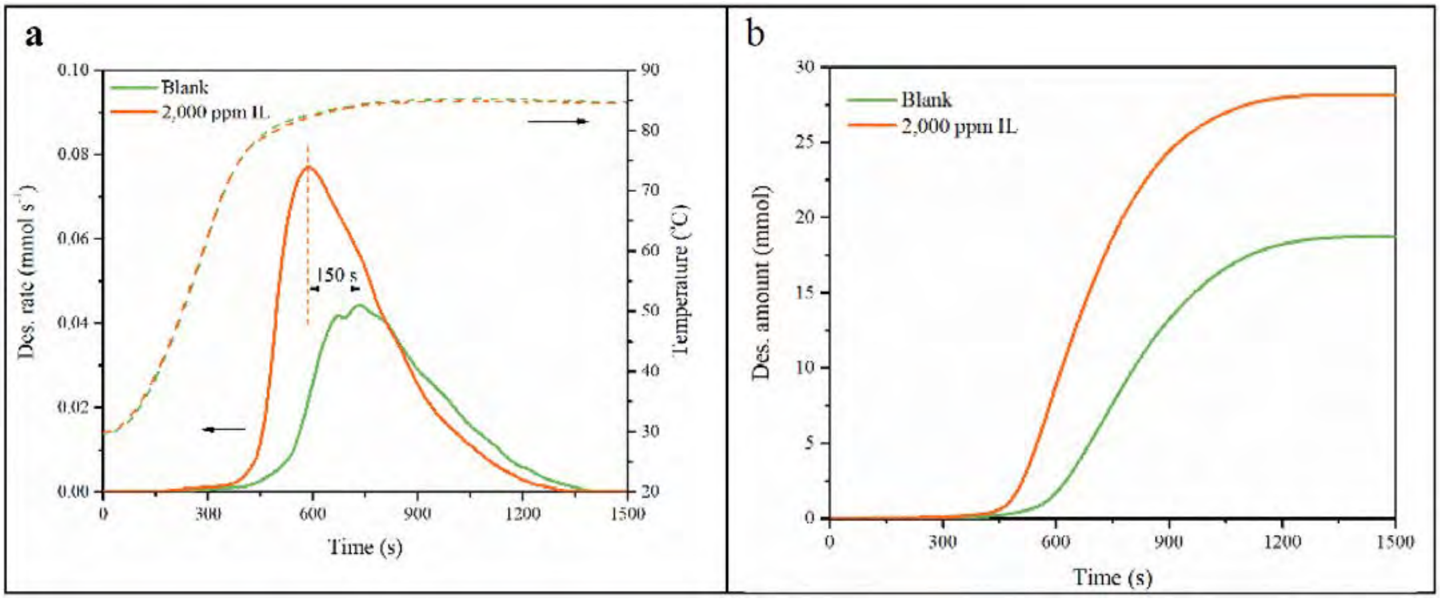

Figure 1: Catalytic effect of IL on CO_2 absorption and desorption. (a) Effect of CO_2 desorption rate with and without catalyst; (b) effect of catalyst on the quantities of desorbed CO_2.

The desorption rate improvement obtained with the IL catalyst can reach as high as 175% (Figure 1a, 0.07 mmol s^{-1} versus 0.04 mmol s^{-1}), and the time required to reach the maximum desorption rate with the IL catalyst is shortened by 150 seconds (Figure 1a), in comparison with that for un-catalyzed CO_2 desorption. As shown in Figure 1b, the total amount of CO_2 desorbed increased significantly from 18.7 mmol to 28.2 mmol, an improvement of 51% when the IL catalyst was used as an additive to the MEA solvent. These experimental results clearly show that the IL is quite effective for catalyzing the CO_2 absorption and desorption processes.

The long-term stability of the IL catalyst for CO_2 absorption-desorption was studied with 110 cyclic tests in a time period of more than five months. The results of the long-term cyclic testing are shown in Figure 2, which shows that there are no evident changes in both the quantities of absorbed and desorbed CO_2 within the 100 cycles in first-stage testing. The 100 cycles of CO_2 absorption-desorption testing were carried out in a 30-day period. The average working CO_2 capture capacity within the 100 cyclic tests conducted in the 30-day period was 23.2 mmol per 100 mL of solvent, which was very close to the 24.3 mmol per 100 mL of solvent obtained in the first run. The slight decrease was due to the accumulative MEA losses, resulting from the difficulty in condensing and recycling the regenerated MEA in each CO_2 desorption step from the carrier gas stream. It is to be noted that loss of active amine in the solvent will also occur in large-scale industrial applications due to emissions and degradation.

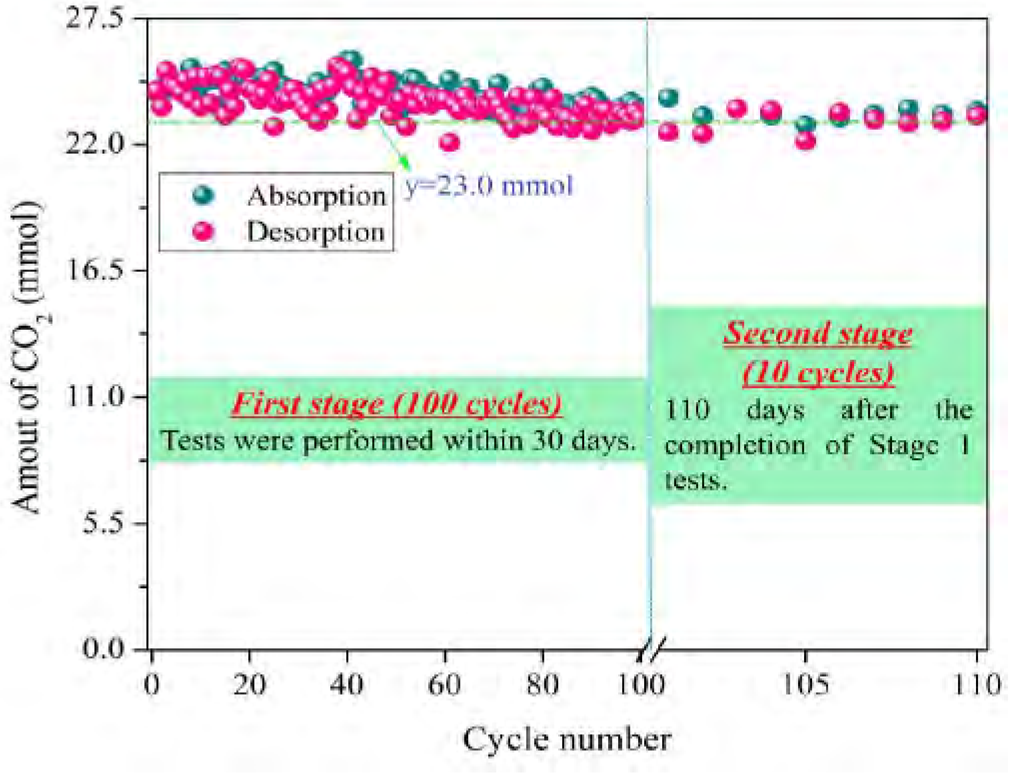

Figure 2: Demonstration of stability of MEA/(EMmim$^+$)(NTF^{2-}) CO_2 capture system in cyclic CO_2 absorption-desorption tests for more than five months.

To further confirm the outstanding stability of the MEA/IL-based CO_2 capture solvent, 10 more cyclic or Stage 2 tests were performed after 110 days after completion of the first 100 cycles or Stage 1 tests by using the same MEA/IL solvent used in Stage 1 tests. For Stage 2, each of the cyclic test results are shown in Figure 2, where it can be seen that the average working CO_2 capture capacity was 23.0 mmol/100 mL solvent, which represents only a 1.7% decrease compared to that obtained in Stage 1. These data confirm the mixture MEA and the IL catalyst is highly stable for long periods of time with outstanding CO_2 capture performance, even though the test gas stream contained 10% O_2.

This impressive reproducibility of the CO_2 capture performance is a direct result of the stability of the catalytic CO_2 capture solvent system. Much milder CO_2 desorption temperatures (85°C), adopted in this case due to increase in CO_2 desorption rate by the use of the IL as a catalyst, further contributed to the stability of this solvent system. Thus, the chemical reversibility of both MEA and the catalyst can be easily realized for the tested CO_2 absorption and desorption temperatures (~30°C and 85°C, respectively). It should be noted that the IL catalyst is thermally stable at temperatures as high as 300°C, as shown by thermal gravimetric analysis (TGA) results in Figure 3.

Amine-modified sorbents are being used in this project as the starting materials because their reaction with CO_2 can be catalyzed by the IL in a similar way as shown above for amine solvent; this is because the reaction mechanism between amine and CO_2 are the same. These sorbents can be prepared by physically impregnating amines into porous support materials, or by chemically grafting the amine functional group onto the support surfaces, stabilizing the sorbent during regeneration. Global Thermostat, a DAC company, has patented a preparation method of using aziridine to obtain hyper-branched amino-silica (HAS) materials, resulting in high loadings of stable amine functional groups. The catalysts can be added to essentially any amine-functionalized sorbent for improved adsorption and desorption kinetics, leading to much higher CO_2 working capacity and much lower temperature for sorbent regeneration. This, in turn, leads to lower regeneration energy consumption and the possibility of using waste heat for desorption of these sorbents, thus significantly reducing the cost of DAC. In this project, two representative amine-modified sorbents will be selected, such as PPI- or PEI-impregnated fumed silica (SiO_2).

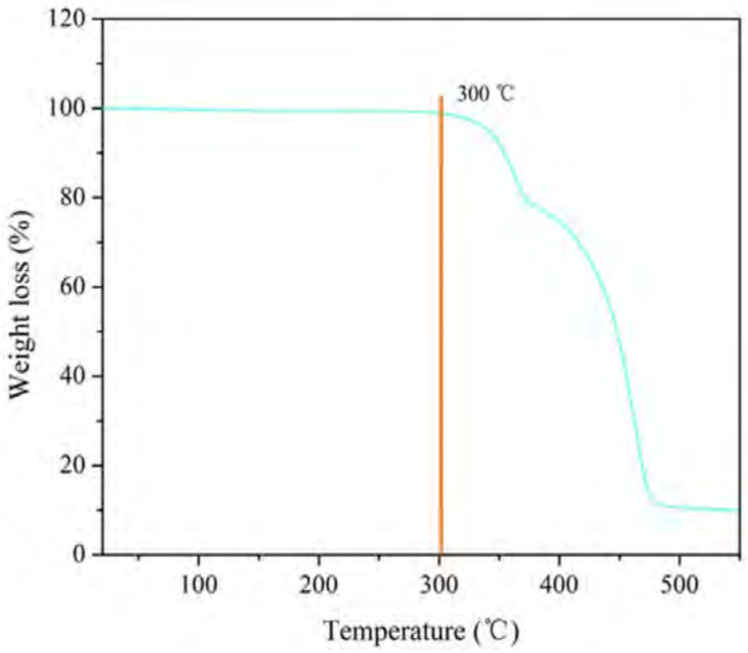

Figure 3. The TGA trace of (EMmim$^+$)(NTF^{2-}) at 10°C heating rate.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,700	1,700
Bulk Density	kg/m^3	400	400
Average Particle Diameter	mm	0.1 – 0.2	0.1 – 0.2
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density	m^2/m^3	2,000 – 3,000	2,000 – 3,000
Solid Heat Capacity @ STP	kJ/kg-K	1.6	1.6 – 2.0
Crush Strength	kg$_f$	N/A	N/A
Attrition Index	-	N/A	N/A
Thermal Conductivity	W/(m-K)	0.2 – 0.3	0.2 – 0.3
Manufacturing Cost for Sorbent	\$/m^3	41,000	40,000
Adsorption			
Pressure	bar	1 – 1.1	1 – 1.1
Temperature	°C	45	45
Equilibrium Loading	g mol CO_2/kg	1.1 – 1.6	1.1 – 1.6
Heat of Adsorption	kJ/mol CO_2	80	80
CO_2 Adsorption Kinetics	gmol/time	1.0	2.0
Desorption			
Pressure	bar	0.9	0.9
Temperature	°C	100 – 120	85
Equilibrium CO_2 Loading	g mol CO_2/kg	0.2	TBD
Heat of Desorption	kJ/mol CO_2	80	80
CO_2 Desorption Kinetics	gmol/time	N/A	3.0

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

	Composition						
	vol%					ppmv	
Pressure	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	0.04	variable	78.09	20.95	0.93	trace	trace

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	143	100
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	52	52
Operating Expenditures	\$/tonne CO_2	91	48

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

technology advantages

- Platform technology for enhancing performance of all amine-based CO_2 DAC systems.
- Catalyst can be added to any amine-based sorbents or solvents for improved sorption and desorption kinetics.
- Low-risk technology that can be applied to existing low-pressure-drop contactor designs.

- The sorbent-based process enables a reduction in the energy required for sorbent regeneration and increased sorbent lifetime/stability due to operation at lower desorption temperatures.

R&D challenges

- Developing an IL catalyst that can be added to amine-doped DAC sorbents to increase desorption kinetics.
- Developing sorbents with low regeneration temperature and low regeneration energy for direct air capture of CO_2.

status

Susteon's patented IL catalyst has demonstrated improvement in CO_2 adsorption capacity of amine sorbents by approximately 50%, with much longer breakthrough times. This catalyst-sorbent combination also improved desorption rate by up to 80%. Susteon also successfully scaled-up catalyst production to kilogram scale. A preliminary technology maturation plan (TMP) was completed, DAC process cost parameters were analyzed, the catalyst synthesis recipe was defined, and quality control procedures were established. Current work involves screening synthesized sorbents through testing at DAC operating conditions.

available reports/technical papers/presentations

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," Project kickoff meeting presentation, Pittsburgh, PA, October 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11092&filename=Low+Regeneration+Temperature+Sorbents+for+Direct+Air+Capture+of+CO2.pdf*.

James Zhou, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Zhou.pdf*.

James Zhou, Maohong Fan, "Low Regeneration Temperature Sorbents for Direct Air Capture of CO_2," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Zhou.pdf*

Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability

primary project goal

The University of Akron, in partnership with Aspen Aerogels Inc., is developing novel solid sorbent materials that can be regenerated in a low vacuum swing adsorption (VSA) process with greater performance than current state-of-the-art materials for the capture of carbon dioxide (CO_2) from air.

technical goals

- Prepare amine-functionalized aerogel.
- Fabricate and test a hierarchical structure of gradient amine sorbent on carbon fiber.
- Construct a VSA test apparatus.
- Conduct sorbent characterization and performance testing.
- Conduct high-level process design and analysis to evaluate feasibility of applying the new sorbents in a direct air capture (DAC) system.

technical content

A hierarchical structure of gradient amine sorbent, which allows CO_2 to adsorb in the form of weakly adsorbed CO_2, will be constructed in bead form. The weakly adsorbed CO_2 can then be regenerated from the sorbent by applying a low vacuum. The novel sorbent allows VSA to be operated at ambient temperature without a significant energy demand, eliminating the energy-intensive heating and cooling cycle in temperature swing adsorption (TSA) processes. Operation at ambient temperature also eliminates the possibility of thermal degradation of sorbents, leading to a prolonged lifetime of the sorbent and minimizing maintenance costs to provide a cost-effective approach for DAC.

To mitigate the corrosive nature of liquid amine sorbents and solvent loss, and to enhance the rate of adsorption/desorption, immobilization of organic amine on high surface area/porous solid has been shown to hold a great promise for replacing the liquid amine process. Many studies have suggested the mechanism of CO_2 adsorption/desorption on solid amines resembled that of CO_2 adsorption in liquid amines. The overall reactions involved in the adsorption/desorption process can be described by the following:

$$2\ R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^- \text{ (carbamate ion) (1)}$$

$$R_1R_2NH + H_2O + CO_2 \leftrightarrow R_1R_2NH_2^+ + HCO_3^- \text{ (bicarbonate) (2)}$$

$$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^-H^+ \text{ (carbamic acid) (3)}$$

In absence of water (H_2O) vapor, one mole of CO_2 reacts with two moles of amine to form carbamate by reaction (1); in presence of H_2O vapor, one mole of CO_2 reacts with one mole of amine to form bicarbonate by reaction (2). Recently infrared spectroscopic studies conducted by the University of Akron (Akron), as well as a number of in-depth spectroscopic studies, have shown that CO_2 adsorbs

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine-Based Aerogel Sorbents for DAC

participant:
University of Akron

project number:
FE0031958

predecessor projects:
N/A

NETL project manager:
Carl Laird
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principal investigator:
Steven Chuang
University of Akron
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partners:
Aspen Aerogels Inc.

start date:
01.01.2021

percent complete:
67%

on the immobilized amine (i.e., solid amine) as carbamic acid and ammonium carbamate ions (i.e., the same type of carbamate ion as the liquid organic amine in the aqueoussolution). Because of an insufficient amount of adsorbed H_2O and the lack of mobility of amine sites, bicarbonate was produced at a negligible level on immobilized amine.

Development of Pellets for TSA with Fixed Bed and Fluidized Bed

Akron has developed a number of immobilized amine sorbents for TSA processes. Collaboration with Aspen Aerogels (Aspen) led to the development of a robust sulfur-resistance sorbent for TSA. Akron has also developed a sorbent for fixed and fluidized beds. The infrared spectra in Figure 1 shows these sorbents containing primary amine at 3,297 and 3,355 cm^{-1}. The secondary amine at 3,297 cm^{-1} capture of these sorbents and their CO_2 binding energy, as well as their resistance to degradation, are strongly dependent on many factors, such as the type of amine (i.e., primary, secondary, and tertiary) and their loading, overlapped with the asymmetric vibration of the primary amine. The sulfur resistant amine (KD-SRE) sorbent containing Aspen's hydrophobic aerogel produces a smaller water band in the 3,100–3,700 cm^{-1} region. These results show Aspen's amine-functionalized aerogel is able to impart hydrophobicity to the amine sorbent. The carbon dioxide adsorbed in the form of ammonium ions at 1,668 cm^{-1} and carbamate ion at 1,510 cm^{-1}. Evacuation of adsorbed CO_2 at 8 pounds per square inch (psi) at 25℃ for three minutes by vacuum led to a decrease in the infrared intensity of adsorbed CO_2, indicating a weakly adsorbed CO_2, which may be removed without heating. More than 60% of adsorbed CO_2 has to be removed from the temperature program desorption (TPD). The sorbent is then returned to the initial state, as shown by its infrared spectra, which exhibited the same feature as the initial spectra. The key feature of TSA sorbents is the requirement of heating to desorption temperature for sorbent regeneration.

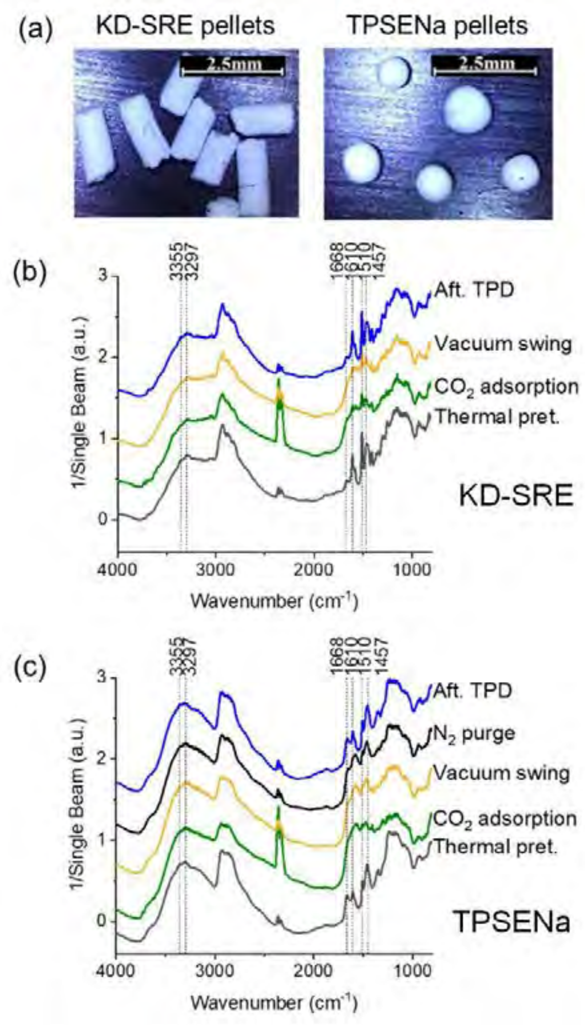


Figure 1 (a) KD-SRE pellets: a sulfur-resistant amine sorbent prepared by incorporation of TPSENa with Aspen's aerogels; TPSENa pellets: a high attrition-resistance sorbent that contains tetraethylenepentamine (TEPA), polyethylene glycol (PEG), epoxy, Na_2CO_3, and SiO_2; (b) (c) infrared spectra.

Vacuum Swing Adsorption

Akron devised a vacuum swing CO_2 capture process for the sorbent that allows CO_2 to adsorb in the form of weakly adsorbed CO_2. Figure 2 compares Akron's VSA process with the TSA process. VSA significantly simplifies the process by eliminating the highly energy-intensive heating and cooling process. Operation at ambient temperature further eliminates the possibility of thermal degradation of the amine sorbents.

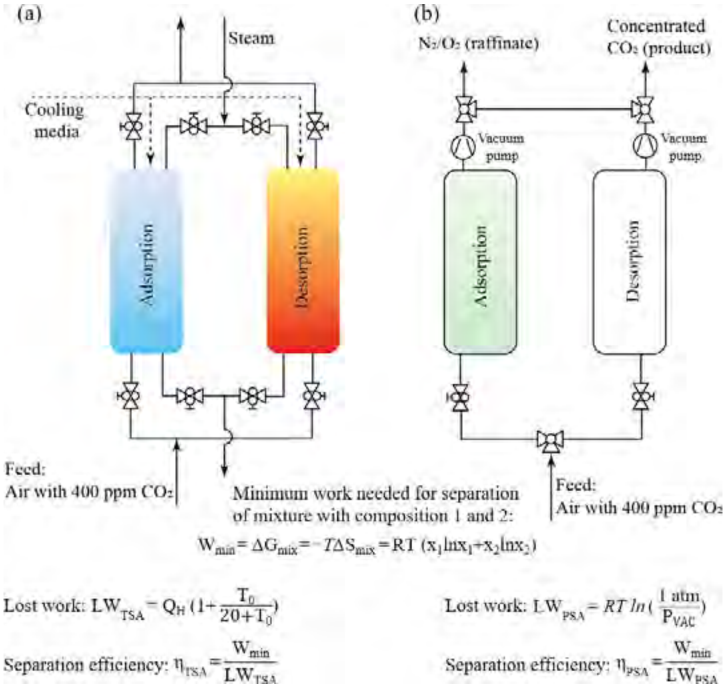
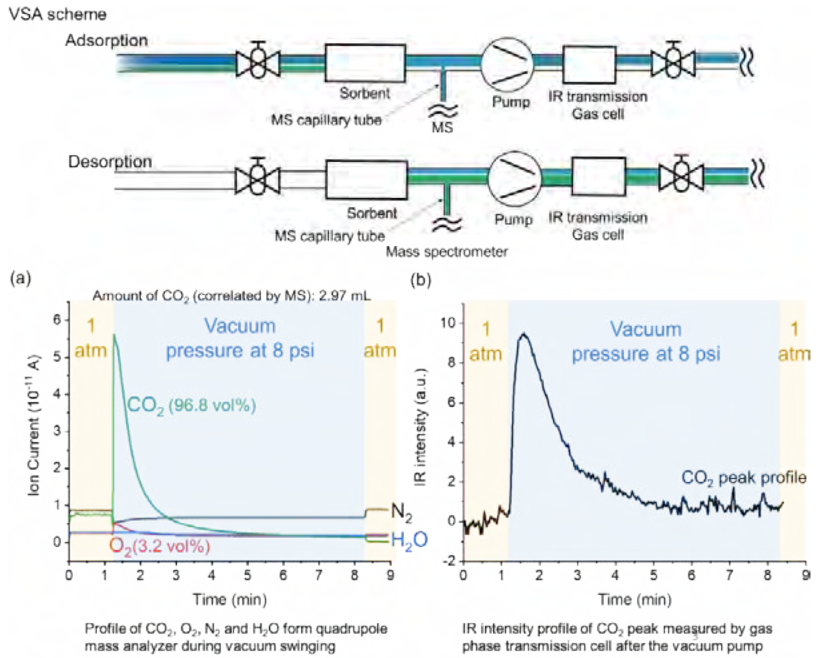


Figure 2 Temperature swing adsorption versus vacuum swing adsorption. (T_0 = heating temperature).

Thermodynamics for TSA and VSA

Minimum work (Wmin) for separation of CO_2 from air is the same for both TSA and PSA. The thermodynamic efficiency of the processes are determined by lost work temperature swing adsorption (LW_{TSA}) and lost work pressure swing adsorption (LW_{PSA}). The absence of thermal energy term (Q_H) in the separation efficiency of the pressure swing adsorption (ηPSA) equation leads to lost work being greater than that of the TSA (ηPSA > ηTSA). LW_{PSA} is a result of using a mechanical pump to evacuate gaseous species to drive the desorption of weakly adsorbed CO_2. Lowering the pressure from 1 atm (760 torr) to 8 psi (413 torr), LW_{PSA} = 1,563 kJ/mol of gas, the operation efficiency can vary from more than 90% to less than 80%, depending on the level of vacuum. Therefore, decreasing the solid volume (i.e., the amount of gas to be evacuated) in the VSA unit can increase the efficiency of the VSA system; however, it will affect the kinetics of adsorption and desorption, as well as the pressure drop of the air flow during CO_2 adsorption. Akron has also observed a 2–3°C drop in temperature during CO_2 desorption of weakly adsorbed CO_2 and then a return to the initial sorbent bed temperature under argon purge, revealing the sorbent bed adsorbs the energy from the ambient. Thus, it is essential to incorporate highly thermal co-conductive materials in the sorbent to facilitate the heat transfer and desorption.

Figure 3 illustrates the VSA results on previous TSA sorbents that were selected for their high capacity of weakly adsorbed CO_2 for the preliminary study. In a typical VSA, CO_2 adsorption was carried out by flowing CO_2-containing stream over the sorbent bed. Instead of heating for sorbent regeneration and collection of both weakly and strongly adsorbed CO_2 with steam or purge gas, VSA removes weakly adsorbed CO_2 at ambient temperature with low pressure. In this specific experiment, closing the inlet valve of the sorbent bed and applying the low pressure at 8 psi led to the removal of weakly adsorbed CO_2. (Note that 1 atm=14.7 psi) Figure 3(a) shows the mass spectrometer (MS) composition profile of the gaseous stream during evacuation of weakly adsorbed CO_2 on a KD sorbent (an amine-functionalized aerogel prepared by Aspen Aerogels Inc.). Figure 3(b) shows the infrared profile of gaseous CO_2 emitted from the vacuum pump. The infrared profile of CO_2 is broader than the MS profile of CO_2 because of the transportation lag resulting from the gaseous line and the vacuum pump. The MS profile showed a highly concentrated CO_2 mole fraction of 96.8%, with a low concentration of nitrogen (N_2) and oxygen (O_2), as determined by the areas under their corresponding MS profiles in Figure 3(a), demonstrating the technical feasibility of VSA using sorbent with weakly adsorbed CO_2.



Profile of CO_2, O_2, N_2 and H_2O form quadrupole mass analyzer during vacuum swinging

IR intensity profile of CO_2 peak measured by gas phase transmission cell after the vacuum pump

Sample	Capture capacity (mmol/g)	Weakly adsorption percentage	
		Vacuum swinging	N_2 purge
TPSENa	3.4	18.84%	24.76%
KD-240-24-9B sorbent	2.0	55.55%	/

Figure 3. VSA Scheme—Adsorption by flowing a 0.04% CO_2 stream over a sorbent bend; desorption of weakly adsorbed species by vacuum. The concentration profiles of the effluent form adsorption bed under 8 psi vacuum determined by (a) MS before vacuum pump, (b) infrared gas cell after vacuum pump. (1 atm=14.7 psi)

CO_2 Capture VSA Unit

The need for processing a large volumetric flow of air with a dilute concentration of CO_2 around 420 parts per million (ppm) presents a monumental challenge to the development of a sustainable and cost-effective CO_2 capture process. The current liquid monoethanolamine (MEA) technology is cost-effective for separation of CO_2 from natural gas in liquefaction and ammonia synthesis processes because of the value of their end products. This technology, when applied for capture of CO_2 from coal-fired power plants, increases the cost of electricity by more than 70%. Application of MEA technology to a dilute stream is not economically feasible in the foreseeable future. In spite of extensive research and development on immobilized (i.e., solid) amines and their attractive features, the employment of solid amines in TSA CO_2 capture has not been successful because of sorbent degradation and low CO_2 capture capacity. In addition, the cost of energy-intensive heating and cooling in TSA is nearly insurmountable.

Recent studies conducted by Akron have shown that amine sorbents aiming at TSA CO_2 capture consists of strongly and weakly adsorbed CO_2. The availability of weakly adsorbed CO_2 to be removed under a purge gas flow and vacuum at ambient temperature for sorbent regeneration provides a unique opportunity to utilize low vacuum for a VSA CO_2 capture process.

Figure 4 illustrates the approach to develop a cost-effective VSA CO_2 capture process. Figure 4(a) show a cascade VSA process consisting of two VSAs in a series, which allows concentrated CO_2 from the first VSA to be further concentrated in the second VSA. Air stream will be diverted to parallel VSA units for semi-continuous processing, where one VSA unit will be operated at the adsorption stage and the other unit will be operated at the desorption stage (i.e., under vacuum). Preliminary estimation showed that a 1-kg VSA unit will be able to process 200 liters per minute for five minutes for CO_2 adsorption to saturate amine sites at ambient condition (room temperature and one atm).

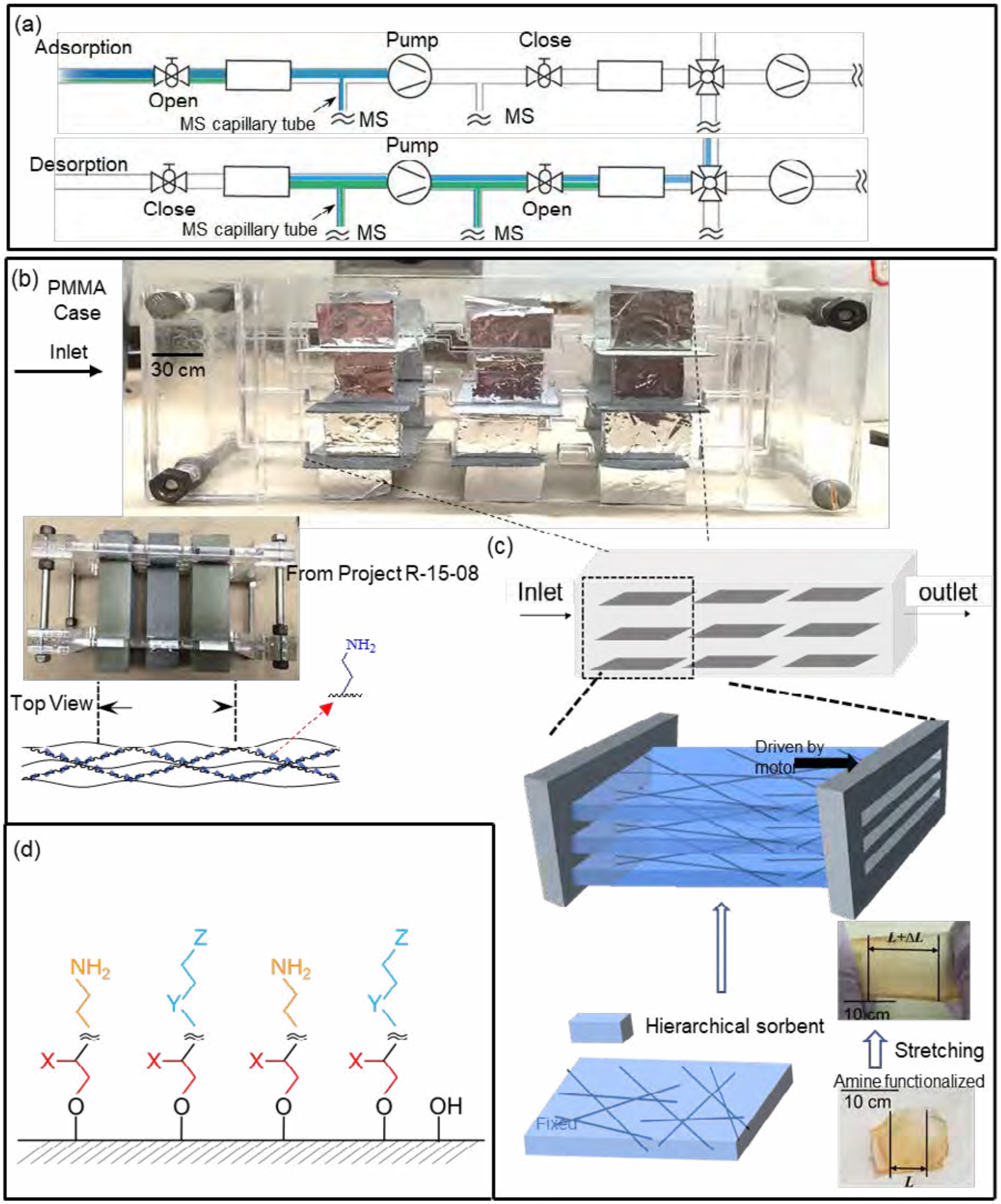


Figure 4. Vacuum swing adsorption for CO_2 capture from air (a) VSA scheme, (b) a VSA unit with sorbent plates in a plexiglass (i.e., PMMA) case, (c) the arrangement of sorbent plates in a parallel configuration, (d) the structure of amine sites for weakly adsorbed CO_2. X, Y, and Z denote different types of functional groups.

Figure 4(b) shows the CO_2 VSA unit Akron has designed and built on plexiglass (i.e., Poly(methyl methacrylate): PMMA). This unit was previously built for an electrically heated TSA process and consists of a set of monolithic rectangular plates of sorbent with dimensions of 20 cm x 10 cm x 0.1 cm, shown in Figure 4(c)/(d). The new sorbent plates manufactured with a low-cost carbon fiber provides mechanical strength. Amine sorbent particles were adhered on the carbon fiber with a porous adhesive. The use of parallel sorbent plates allows for the processing of a large volume of air flow with a minimum pressure drop and diffusion limitation. Porous polymer with a surface area greater than 350 m^2/g will be used to support the amine sites, shown in Figure 4(d). Akron has prepared sorbent pellets at kg-scale for previous TSA CO_2 capture processes. This preparation method, which was tuned for mechanical strength for a fluidized bed operation, are being tuned for high surface area since the sorbents in VSA are stationary. Immobilized amine and specific additives will eliminate the migration of amine sites during long-term VSA operation. In summary, the VSA process will allow use of low energy air blower to bring air to contact with VSA sorbent and allow use of low vacuum for collecting weakly adsorbed CO_2.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	910	<800
Bulk Density	kg/m^3	270	260
Average Particle Diameter	mm	0.1	2
Particle Void Fraction	m^3/m^3	0.32	0.5
Packing Density	m^2/m^3	0.7	0.5
Solid Heat Capacity @ STP	kJ/kg-K	2.36	2.2
Crush Strength	kg$_f$	N/A	N/A
Attrition Index (wt% change at 1.4 x fluidization	-	<0.01%	—
Thermal Conductivity	W/(m-K)	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	100	50
Adsorption			
Pressure	bar	1	1
Temperature	°C	25	25
Equilibrium Loading	g mol CO_2/kg	0.7	1
Heat of Adsorption	kJ/mol CO_2	51	45
CO_2 Adsorption Kinetics at the first 3 sec	gmol/sec	1.1	1.1
Desorption			
Pressure	bar	0.1	0.1
Temperature	°C	25	25
Equilibrium CO_2 Loading	g mol CO_2/kg	0.6	0.8
Heat of Desorption	kJ/mol CO_2	51	45
CO_2 Desorption Kinetics at 1 atm	gmol/time	To be determined	0.1

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	77 °F	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Amine-functionalized aerogels have high CO_2 working capacity, low energy sorbent regeneration, high moisture resistance, and long stability over 500 adsorption-desorption cycles.
- Operates at ambient temperature.
- Scalable and modular design.

R&D challenges

- Identification of amine sites for weakly adsorbed CO_2.
- Production of high-purity CO_2 (greater than 99%).
- Fabrication of hierarchical sorbents with a high density of weakly adsorbed CO_2 sites.
- Construction of low leakage vacuum swing unit.

status

The project team developed an amine-functionalized aerogel that was tested in multiple adsorption/desorption cycles in a laboratory-scale (5–10 cm^3) VSA unit. The simultaneous monitoring of the aerogel sorbent using in situ infrared and MS was completed to understand the adsorption and desorption kinetics for both the strongly and weakly adsorbed CO_2. Fabrication and scale-up of a 1-liter VSA unit is currently in progress. Preparation for impregnation of amine-based aerogel into monolith structures is also currently in progress.

available reports/technical papers/presentations

Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11068&filename=Gradient+Amine+Sorbents+for+Low+Vacuum+Swing+CO2+Capture+at+Ambient+Temperature.pdf*.

Steven Chuang, “Gradient Amine Sorbents for Low Vacuum Swing CO_2 Capture at Ambient Temperature,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Chuang.pdf*

Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection

primary project goal

Columbia University, along with project partners Cornell University and Oak Ridge National Laboratory, is developing an intelligently tailored sorbent material using a state-of-the-art anhydrous nanofluid solvent and electrospinning technology to form a hybrid coaxial-fiber system for direct air capture (DAC) of carbon dioxide (CO_2).

technical goals

- Develop novel NOHMs while tuning the CO_2-binding energies that are suitable for DAC; optimize the chemistries of CO_2-binding sites for the minimum parasitic energy consumption.
- Develop the innovative support system based on the fiber-encapsulation technology.
- Design and develop air filter DAC systems consisting of fibers to allow use as an open system, as well as a closed system, with minimum pressure drop.
- Develop an understanding of degradation pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

There is a need for CO_2 capture materials in DAC systems to be further improved to provide better CO_2 capture capacity and long-term durability. The hybrid fiber system being developed in this project employs Columbia University's well-studied, liquid-like nanoparticle organic hybrid materials (NOHMs) embedded in a permeable, hydrophobic, CO_2-selective ceramic or polymeric shell to form a viscosity-controlled sorbent material with improved CO_2 capture kinetics, long-term stability, and reduced energy requirement for sorbent regeneration. The nanofiber-encapsulated sorbent has the ability to selectively reject water while allowing facile CO_2 diffusion, which can lead to a reduction in parasitic energy consumption during pressure/temperature swing desorption. The nanofibers embedded with NOHMs are being used to fabricate air filters, affording the low pressure drop and improved chemical and physical stability that is needed for DAC systems.

The current state of the CO_2 capture material Technology Readiness Level (TRL) is TRL 2; the aim is to achieve TRL 3 by the conclusion of the project. The notion of encapsulated NOHMs follows Columbia University's earlier work where encapsulation of NOHMs in polymeric microcapsules (Figure 1) was investigated. While the initial capture kinetics were fast, it was found that mass transfer limitation does exist at a higher CO_2 loading. Thus, this project is focusing on other novel carrier designs that can provide greater interfacial areas.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Hybrid

project focus:
Hybrid Coaxial-Fiber System for DAC

participant:
Columbia University

project number:
FE0031963

predecessor projects:
N/A

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Columbia University
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partners:
Cornell University; Oak Ridge National Lab

start date:
01.01.2021

percent complete:
63%

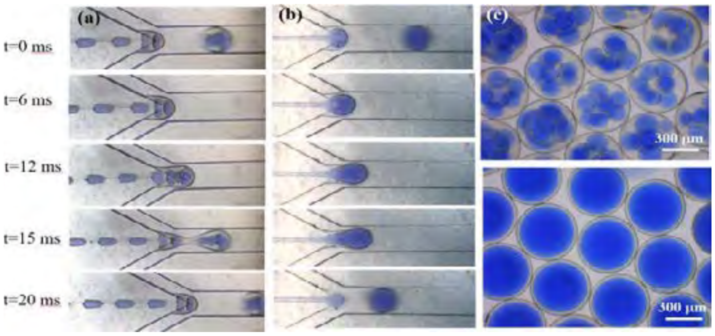

Figure 1: Encapsulated CO_2 capture solvent (NOHMs) produced using a microfluidic device.

The fiber-encapsulation system being studied herein, carrying nanoscale and micronscale droplets of NOHMs in a gas permeable fiber, is highly innovative and has great potential. A fixed-bed CO_2 capture experiment that was recently performed using the encapsulated NOHMs showed that the selection of polymer fiber materials is as important as the NOHMs themselves for DAC with high capacity and high selectivity. Thus, this project is focused on systematically designing NOHM-based hybrid sorbent systems. The approach of encapsulating NOHMs or embedding them in polymer and ceramic fiber matrix provides a transformative multifaceted solution to DAC. The polymer shell provides mechanical strength of NOHM-based sorbents, and can be chemically tuned to selectively reject water. They can also protect NOHMs and reduce the overall parasitic energy consumption of DAC. The design of the DAC unit is flexible (both open and closed systems), allowing potential reduction in the capital and operating costs. There have been no reported studies on fiber-encapsulated anhydrous solvents; thus, if successful, the potential benefits and impact of the technology would be tremendous for DAC.

The tunable nature of the grafted polymeric canopy of hybrid nanomaterials allows for enhanced CO_2 capture capacity and selectivity. The presence of primary and tertiary amines in the polymeric canopy significantly enhances the CO_2 capture capacity ([polyethylene imine (PEI)]-SiO_2 hybrid versus polyetheramine [PEA]-SiO_2 hybrid). In experiments, the amine functional sites of PEI-SiO_2 hybrid reacted with CO_2 to form carbamate species, whereas protonated quaternary amines (as in PEA-SiO_2 hybrid) could not react with CO_2 since they were involved in ionic bonding with the silica nanoparticles (NPs). Overall, a promising CO_2 capture capacity was obtained, exceeding the level commonly reported for monoethanolamine (MEA) solvents.

Solvent impregnated polymers (SIPs) were also considered for the NOHM encapsulation. With this technique, the project was able to encapsulate the pure NOHMs-I-PEI (polyethylenimine functionalized silica nanoparticles) inside a continuous gas permeable polymer matrix (TEGO Rad 2650) as an emulsion phase via shear emulsification and thin polymer film (1-mm thickness) containing microdroplets of NOHMs-I-PEI was produced (Figure 2). Multiple SIP films with different NOHMs-I-PEI loading (9.8–49 wt%) were successfully synthesized and it was observed that the NOHMs-I-PEI droplets (less than 10 μm) are well distributed inside the emulsion phase. Because of the small size of the microdroplets, NOHMs-I-PEI has high interfacial areas enhancing its CO_2 capture kinetics.

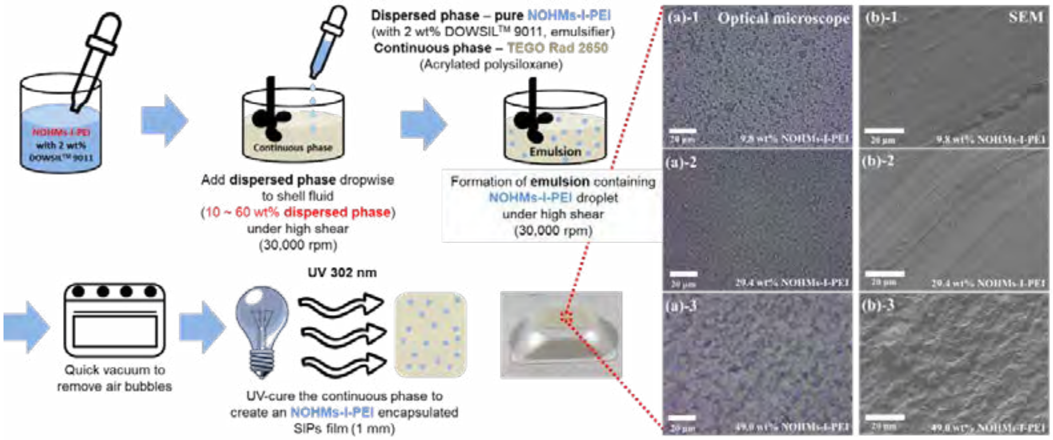

Figure 2: Synthesis of SIPs with NOHMs-I-PEI. (a) Optical microscope images of SIPs and (b) SEM images of the cross-section area of cross-linked SIPs film with different NOHMs loading: 9.8, 29.4, and 49.0 wt%. (Rim, G. et al. *Advanced Functional Materials*, 2021, *31*(21), 2010047)

The CO_2 capture using the SIP films containing 49 wt% NOHMs-I-PEI greatly improved; a remarkable 50-fold increase in CO_2 capture was observed in the SIP films compared to the bulk NOHMs-I-PEI where 5.55 mmol/g of CO_2 uptake capacity was achieved. The combination of liquid-like NOHMs, which has high CO_2 binding energy and highly CO_2 permeable polymer matrix, has a synergetic effect on the absorption of CO_2 by the extremely viscous solvents. Although the slow CO_2 capture kinetics of NOHMs-I-PEI was dramatically enhanced in the SIP films, it was found that its capture kinetics are much slower than particle sorbent systems, which have higher gas-to-solid interfacial area. Therefore, a cryogenic grinding method was used to grind the SIP films and SIP particles (average diameter ($\overline{d^*}$) = 430 μm) resulting in a 49.0 wt% NOHMs-I-PEI powder. The CO_2 absorption performance of the ground SIP particles was evaluated at different temperature conditions (25–100°C) upon exposure to 1 atm CO_2 and compared with the SIP films. The CO_2 uptake kinetics were significantly enhanced by grinding, showing a potential for encapsulation of NOHMs-I-PEI as a solid sorbent. The electrospinning process is proposed as a synthesis route for nanofibers for the encapsulation of NOHMs. Amine-based CO_2 capture materials including NOHMs-I-PEI are typically regenerated at 120°C to break the carbamate bond, which is formed by a rapid chemical reaction between amine groups and CO_2. Stable absorption/desorption behaviors of SIPs containing NOHMs-I-PEI over multiple thermal swing cycles are essential for DAC. As shown in Figure 3, the NOHMs-I-PEI/SIPs showed a great thermal stability over 20 temperature swing (50°C ↔ 120°C) cycles when compared to encapsulated pure PEI (PEI/SIPs) due to the strong ionic bond between the silica nanoparticles and PEI polymer chains. Consequently, the project was able to achieve long-term thermal stability by encapsulating highly viscous NOHMs-I-PEI inside the SIPs.

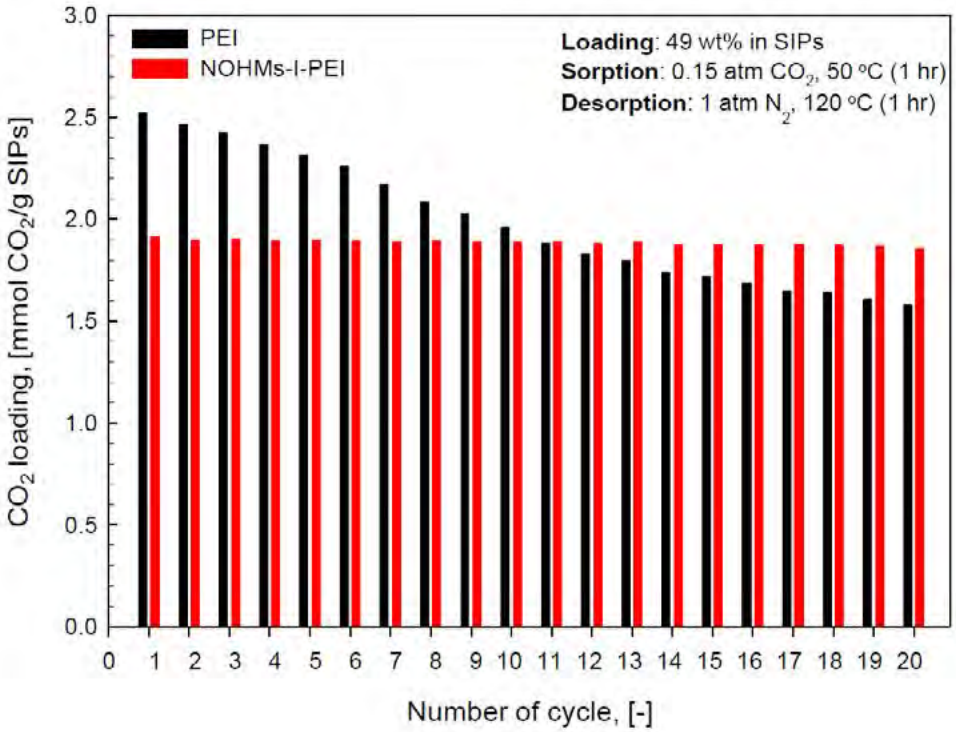

Figure 3: Recyclability of NOHMs-I-PEI/SIPs. (Rim, G. et al. *Advanced Functional Materials*, 2021, *31*(21), 2010047)

Simultaneous CO_2 and moisture capture are inevitable during the DAC process since the water concentration in ambient air is generally about 1%, which is 25-times greater than the CO_2 concentration in ambient air. The co-absorption of moisture along with CO_2 led to the breakthrough time being much longer under the wet condition, leading to increased working CO_2 capture capacity. The theoretical capture capacity of primary and secondary amines was enhanced up to twofold due to bicarbonate formation and the tertiary amines in PEI being able to react with CO_2 forming the bicarbonate in the presence of water.

Cornell has developed scalable, nanomanufacturing processes in advanced materials processing, including nanofiber formation via electrospinning. Based on the understanding of the electrospinning process, a gas-assisted electrospinning (GAES) system was designed to overcome many shortcomings of the conventional electrospinning setup. Utilizing the concentric, coaxial nozzle configuration to synergistically combine high electric field and high-speed air, GAES allows for cost-effective, facile production of polymer, metallic, and ceramic nanofibers and their hybrids and has also been successful in tailoring the placement of nanomaterials in nanofibers. The electrospun nanofibers were collected as randomly oriented non-woven mats on the collector and have been applied in air filtration application. Due to the large surface area of nanofibers and residual electric charges in electrostatically active nanofibers, a significantly enhanced filtration efficiency without increasing pressure drop was observed.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1100	1300
Bulk Density	kg/m^3	660	300
Average Particle Diameter	mm	0.4	0.0001 - 0.005
Particle Void Fraction	m^3/m^3	0	0.25
Packing Density	m^2/m^3	$9x10^3$	$2x10^6$
Solid Heat Capacity @ STP	kJ/kg-K	1.75	1.75
Crush Strength	kg_f	140 MPa	<< 140 MPa
Attrition Index	-	0.05	< 0.1
Thermal Conductivity	W/(m-K)	0.15	15
Manufacturing Cost for Sorbent	$/kg	1100	1300
Adsorption			
Pressure	bar	1	1
Temperature	°C	25	10 - 40
Equilibrium Loading	g mol CO_2/kg sorbent	1.66	2
Heat of Adsorption	kJ/mol CO_2	-85	-85
CO_2 Adsorption Kinetics	gmol/time	0.08 gmol/kg/hr	1.0 gmol/kg/hr
Desorption			
Pressure	bar	0	0
Temperature	°C	120	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.02	0.04
Heat of Desorption	kJ/mol CO_2	85	85
CO_2 Desorption Kinetics	gmol/time	-12 gmol/kg/hr	-20 gmol/kg/hr
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Air filtration media	
Flue Gas Flowrate	kg/hr	n/a	
Space Velocity	hr^{-1}	n/a	
Volumetric Productivity	$gmol_{CO2}/(hr\ l_{absorber\ bed})$	n/a	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— n/a	—
Adsorber Pressure Drop	bar	Negligible	
Degradation	% capacity fade/cycle	n/a	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	n/a	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	**Composition**						
	vol%					ppmv	
14.7 psia	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Chemisorption of CO_2 onto amine-functionalized silica nanoparticles (NOMHs).

Sorbent Contaminant Resistance – Hydrophobic polymeric and ceramic encapsulation materials provide water-rejection while maintaining high CO_2 permeability and selectivity. The hydrophobic surface also allows easy removal of any particles collected onto fibers by washing.

Sorbent Attrition and Thermal/Hydrothermal Stability – PEI-tethered silica (e.g., NOHMs) has been demonstrated to possess enhanced oxidative thermal stability at elevated temperatures with lower capacity loss across multiple cycles, compared to neat PEI. Since the filter design does not require the movement of sorbent, there are no concerns related to sorbent attrition.

Process Design Concept – See Figure 4.

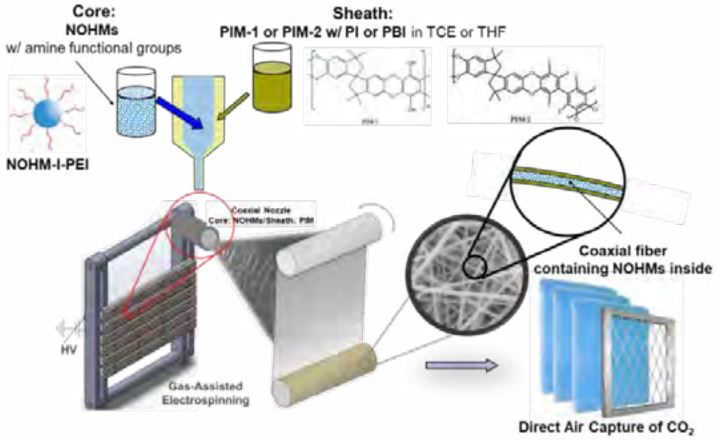

Figure 4: Proposed module design.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	148.12	120
Cost of Carbon Avoided	$/tonne CO_2	21.5 ~ 124 (vary by source)	20 – 100 (vary by source)
Capital Expenditures	$/tonne CO_2	1,280	1000
Operating Expenditures	$/tonne CO_2	88.54	80

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

Calculations Basis – Current R&D values are obtained using the Technoeconomic Assessment Tool for Direct Air Capture (Wilcox, J. et al, March 2020, https://docplayer.net/184810231-Technoeconomic-assessment-tool-for-direct-air-capture-march-2020.html), which is based on the main assumptions outlined in NASEM 2019 Sorbent Mid-Range (https://doi.org/10.17226/25259).

Scale of Validation of Technology Used in TEA – Modeling.

technology advantages

- NOHMs embedded in polymeric nanofibers will offer enhanced capture kinetics and improve the long-term recyclability with minimized sorbent regeneration energy due to hydrophobicity of the polymeric nanofibers.
- NOHMs do not suffer from solvent loss in air streams due to their negligible vapor pressure.
- NOHM-encapsulated nanofibers have a greater interfacial area for enhanced air-NOHM interactions to overcome mass transfer-related issues associated with high viscosity and more flexibility for the reactor design with minimum pressure drop.
- Novel tailored material that incorporates the desirable properties of both liquid-like NOHMs and solid nanofiber sorbents enables ease of deployment, while addressing the challenges with both.

R&D challenges

- Incorporation of NOHM-based hybrid sorbents with electrospun fibers.
- Moving to large-scale production while maintaining higher capture capacity and selectivity, and improved water tolerance.

status

Columbia University has successfully synthesized NOHMs with oxidative thermal stability and optimized techniques to successfully electrospin PIM-1 and PIM-2 fibers in the 0.8-2-micron dimensional range. Encapsulated NOHMs have been tested and have shown promising thermal cyclability and CO_2 capture performance across multiple loading/regeneration cycles. After extensive synthetic optimization, three candidate polymeric materials were identified and selected to encapsulate NOHMs: PIM-1, PIM-2, and TEGO Rad. Work is currently being conducted to electrospin polymeric fiber mats onto coarse filter media for increased structural stability.

available reports/technical papers/presentations

Ah-Hyung (Alissa) Park, “Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection,” Direct Air Capture Kickoff Meeting presentation, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Park.pdf*.

Ah-Hyung (Alissa) Park, “Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection,” 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Park.pdf*.

Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Fibers

primary project goal

The State University of New York (SUNY)-Buffalo is teaming with Arizona State University (ASU) and Gas Technology Institute (GTI) to develop an innovative sorbent comprised of trapped small amines in hierarchical nanoporous capsules (HNCs) embedded in porous electrospun fibers (PEFs) for direct air capture (DAC). The effective encapsulation of amines in HNCs will enable high sorbent stability and the innovative PEF macroscopic scaffold will allow for fast exposure of sorbent material to air. Research efforts involve the tailoring of both sorbent and PEF materials to achieve a compact system for DAC with high capacities for carbon dioxide (CO_2) at concentrations typically available in air and at near-ambient conditions.

technical goals

- Develop HNCs with trapped small amines sorbents (SUNY-Buffalo).
- Incorporate the sorbent material into PEFs (Arizona State University).
- Test the PEFs with the embedded sorbent material to collect data on CO_2 working capacity and adsorption/desorption rates (SUNY Buffalo).
- Utilize the experimental data obtained to perform high-level process design/analysis.
- Develop an understanding of breakdown pathways; confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

An innovative sorbent structure is being designed to directly capture CO_2 from the air using trapped small amines (Figure 1). This technology differs from the sorbents for CO_2 capture at higher CO_2 partial pressure by physical adsorption, in that approximately 400 parts per million (ppm) CO_2 in the air is adsorbed into the HNCs and reacts with trapped amines, following the reactions below:

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Amine Sorbent Embedded in Porous Electrospun Fibers for DAC

participant:
State University of New York (SUNY)-Buffalo

project number:
FE0031969

predecessor projects:
N/A

NETL project manager:
Dustin Brown
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Miao Yu
State University of New York (SUNY)-Buffalo
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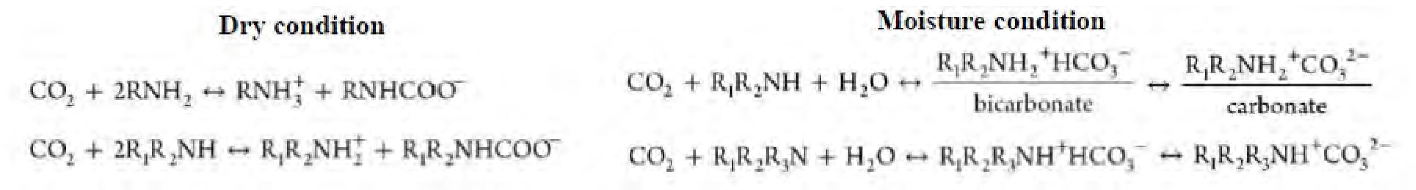
partners:
Arizona State University; Gas Technology Institute (GTI)

start date:
02.01.2021

percent complete:
60%



Dry condition

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^-$$

Moisture condition

$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underset{\text{bicarbonate}}{R_1R_2NH_2^+HCO_3^-} \leftrightarrow \underset{\text{carbonate}}{R_1R_2NH_2^+CO_3^{2-}}$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3^- \leftrightarrow R_1R_2R_3NH^+CO_3^{2-}$$

Therefore, theoretically, two amine groups can bond with one CO_2 molecule under dry conditions and one amine group with one CO_2 under wet conditions. Small amines enable high amine efficiency (molar ratio of the adsorbed CO_2 to the total amine groups, CO_2/nitrogen [N]) and thus high CO_2 adsorption capacity from the air, while HNCs prevent amine loss and drastically extend amine lifetime. Small-sized (2–5 µm), macroscopic scaffold PEFs allow fast external mass transfer rates and minimize CO_2 adsorption capacity loss via high porosity. In addition, optimized packing of PEFs in a mat (Figure 1) ensures high sorbent packing density while balancing the air flow rate with the energy consumption from the blower.

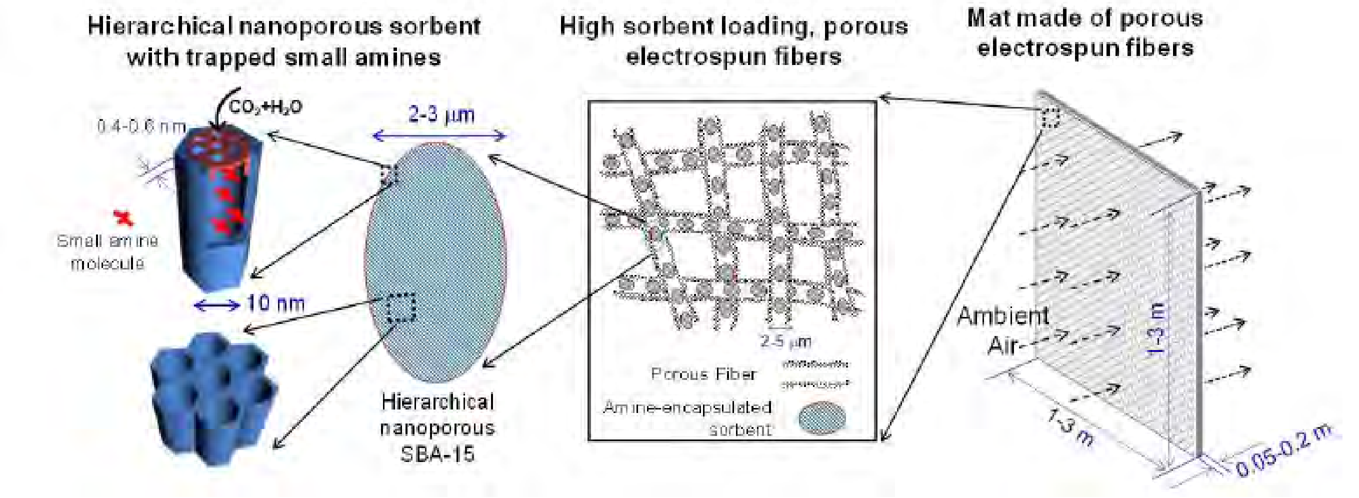


Figure 1: Diagram of the transformational adsorbent for direct capture of CO_2 from air.

These mats are effectively utilized in a process for direct CO_2 capture from the air, as shown in Figure 2. For each operation unit, there are two components: a blower and a sorbent mat equipped with heat exchanger, heating wires, and a hinged cover for mat sealing. Each unit has three operational modes: adsorption, preheat, and desorption. During the process, each unit finishes one operational mode and enters another operational mode. Note that depending on the available sources of energy input, desorption energy can be provided by either electricity or waste heat.

Amine-functionalized sorbents and ion-exchange resins are the promising sorbents reported in the literature for DAC; the former can achieve much higher CO_2 purity (greater than or equal to 98 vol.%) than the latter (less than 5 vol.%). In amine-based sorbents, large surface-area porous substrates are usually used to increase the loading of amines and thus the amine group density; amines with different molecular structures are also used to increase efficiency. The combination of the amine group density and amine efficiency leads to a high CO_2 adsorption capacity. Depending on the interaction between the amines and substrates, three types of sorbents (Types I: physical impregnation; Type II: covalent tethering via silane linkage; Type III: direct covalent tethering via in situ polymerization) can be prepared, as shown in Figure 3.

Figure 4 plots the CO_2 equilibrium capacity versus amine efficiency of the sorbents described above. As shown, the efficiencies are lower than 0.2, far below the theoretical 0.5 (dry condition) and 1 (moisture condition). In the sorbent structure being designed in this project, small amines are featured with fast reaction kinetics and high concentration of amine groups and are expected to have high CO_2 capacity and fast adsorption rate, making them ideal amines for DAC. In addition, small amines typically show high amine efficiency (e.g., diethanolamine [DEA] shows an efficiency of 0.407, very close to the theoretical value [0.5]). In the technology for this project, small amines are loaded and trapped in SBA-15 (a mesoporous form of silica with approximately 10 nm pores and a high surface area of 600–1,000 m^2/g). Assuming 30–50 wt.% amine loading, 0.4–0.6 amine efficiency (in humid air), and four amine groups in one amine molecule (molecular weight: 200 g/mol), the estimated CO_2 capacity of the sorbent is in the range of 3.4–13.3 mmol CO_2/g (Figure 4). This is much higher than reported results, demonstrating the great potential of small amines for DAC.

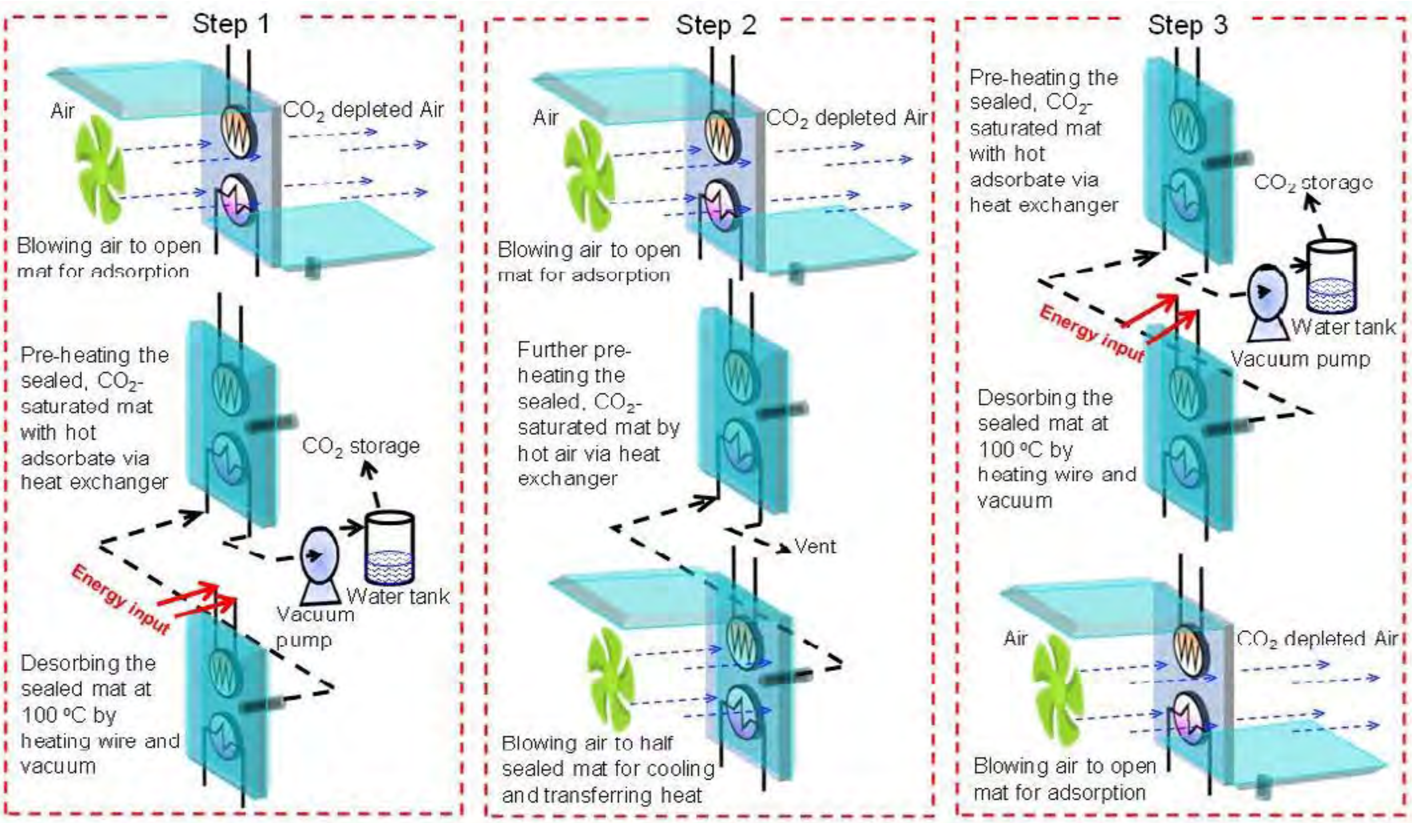


Figure 2: Diagram of the process for DAC.

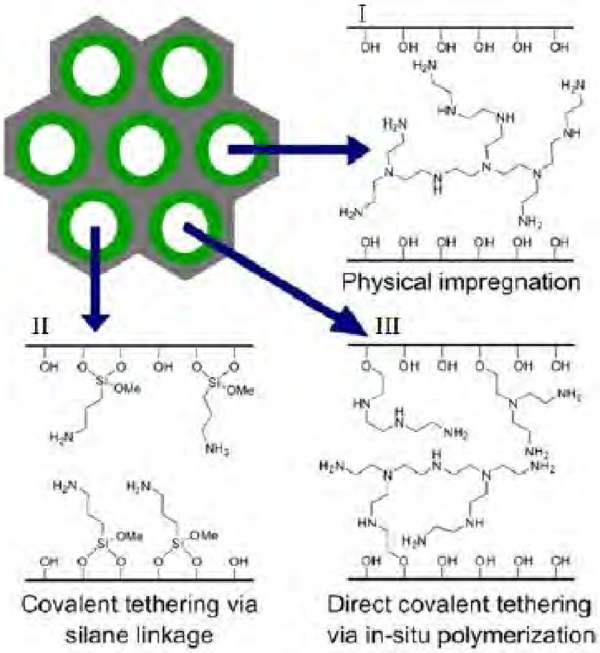


Figure 3: Schematic of three types of amine-based sorbents for DAC.

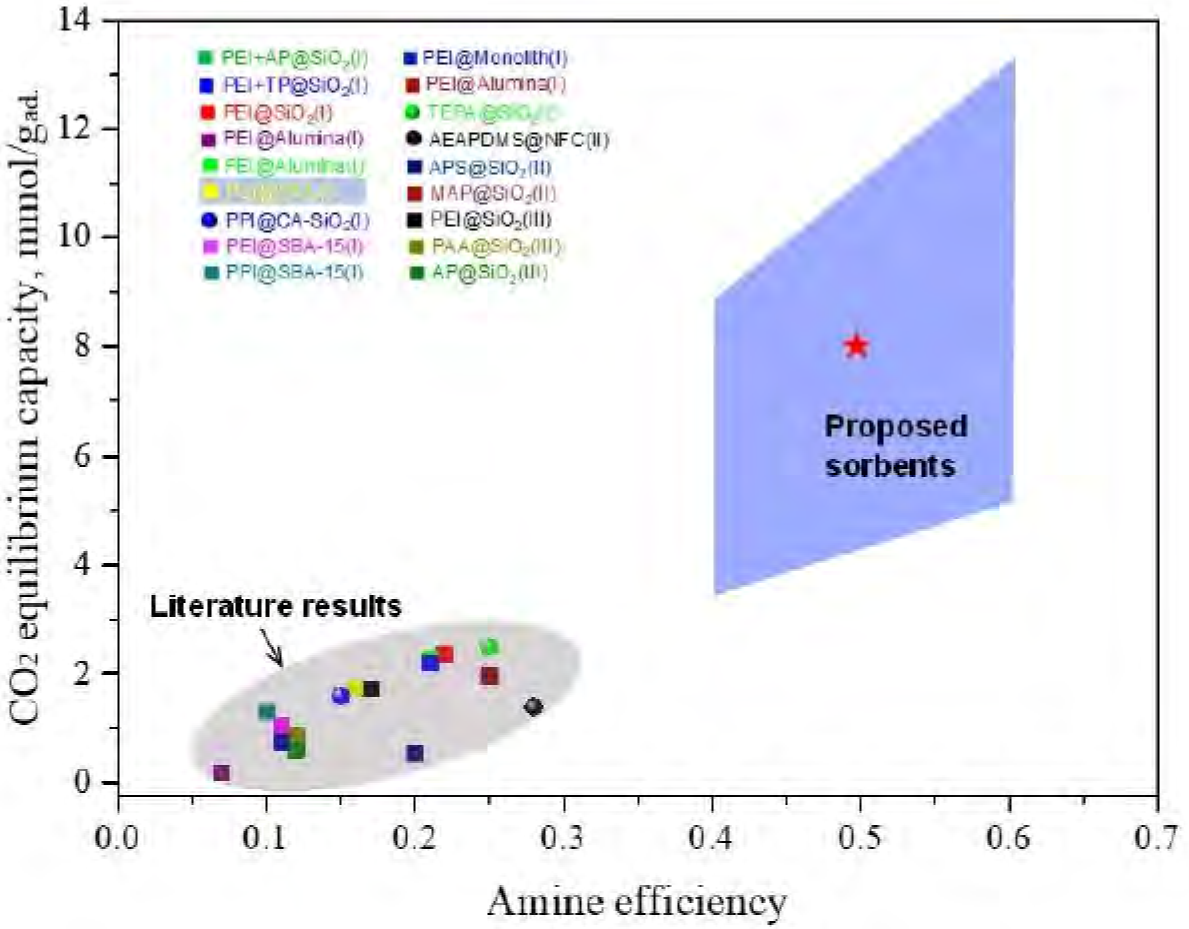


Figure 4: Comparison of reported sorbent materials and projected performance of the proposed sorbent for DAC. Red star represents the average performance of the proposed sorbent.

Small amines, such as monoethanolamine (MEA) and DEA, have been widely used for solvent-based CO_2 capture/removal due to their fast reaction rate with CO_2 and high CO_2 capacity. Small amines on porous substrates exhibited excellent CO_2 adsorption performance: fast CO_2 uptake rate, high amine efficiency (e.g., 0.4–0.6 for DEA), high CO_2 adsorption capacity resulting from the high nitrogen to carbon (N/C) ratio, high primary amine concentration, and low viscosity. However, high volatility of small amines led to severe loss during the sorbent regeneration at high temperature, which significantly restricted their application in sorbent materials. Physically trapped small amines in porous structure using an innovative interfacial reaction process is expected to resolve the amine loss issue.

SUNY-Buffalo recently developed a facile and scalable interfacial reaction process to deposit ultra-thin, microporous coatings on nanoporous substrates for trapping/encapsulating functional species. A mesoporous silica, SBA-15, was used as the porous substrate, and a microporous coating layer of titanium dioxide (TiO_2) was deposited by the liquid-liquid interfacial reaction between ethylene glycol (EG) and titanium chloride ($TiCl_4$) and subsequent calcination to remove the organic compound. Microporous coating pore size can be adjusted by adding different amounts of water in EG and by changing calcination conditions. The microporous TiO_2 coating on SBA-15 was characterized by transmission electron microscopy (TEM), which showed that a continuous, ultra-thin TiO_2 layer (30–50 nm) can be seen on SBA-15 after the coating process. Thermogravimetric analysis (TGA) showed the material was thermally stable to at least 300°C (data not shown). These results clearly showed that hierarchical SBA-15 can be formed by facile interfacial reaction process and can effectively trap functional species. To trap small amines with molecular size of 0.5–0.8 nm, a well-designed interfacial reaction process is applied to form coatings with pores larger than CO_2 (0.33 nm) and H_2O (0.26 nm), but smaller than the amine molecules. Because of the strong affinity of CO_2 with small amines, the adsorption selectivity of CO_2 over N_2 is expected to be high. Studies have shown the CO_2 working capacity is much higher than the amount of N_2 adsorbed. Therefore, very high CO_2/N_2 selectivity can be achieved, and CO_2 purity higher than 99% can be obtained after sorbent regeneration.

HNCs can be fabricated by utilizing interfacial reactions followed by calcination. Depending on metal precursors and organic precursors, a hybrid dense layer with different composition can be formed and subsequently converted into microporous coatings by removal of the organic compound upon calcination. The team fine-tuned coating pore size by changing the calcination conditions and adding different amounts of H_2O into EG; coating pore size was characterized by N_2 adsorption at 77K.

Recently, ASU has developed PEFs embedded with various sorbent materials (metal-organic frameworks [MOFs], zeolites, and resin particles) and applied them for separation applications, including DAC. Matrimid (glass transition point: 320°C) and polystyrene (glass transition point: 100°C) with excellent thermal, mechanical, and chemical stabilities have been used as the PEF materials. PEFs with different porosity, morphologies, and post-synthetic modifications have been prepared. The technique to controllably create porosity on PEFs, called solvothermal polymer additive removal (SPAR), has been demonstrated in a preliminary study of uniaxial electrospinning technique. The mechanical and chemical strength of PEFs embedded with sorbent materials can also be improved by a cross-linking process that has been previously demonstrated. In previous work, PEFs embedded with ion-exchange resin have been demonstrated for DAC application by moisture swing adsorption and showed the highest cycle capacity with an uptake rate of 1.4 mmol CO_2.

TABLE 1: ATMOSPHERIC AIR FEED-GAS CONDITIONS

Pressure	Composition						
	vol%					ppmv	
14.7 psia	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
	0.04	variable	78.09	20.95	0.93	trace	trace

Chemical/Physical Sorbent Mechanism – Trapped amines inside the hierarchical nanoporous capsules react with low concentration of CO_2 (~400 ppm) in the air for high-capacity CO_2 capture.

Sorbent Contaminant Resistance – Resistance of the sorbent to trace sulfur oxide (SO_X) and nitrogen oxide (NO_X) is not clear at this stage, but resistance to other components is expected to be good.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition is not clear at this stage. The thermal/hydrothermal stability of the sorbent is expected to be excellent under DAC operation.

Flue Gas Pretreatment Requirements – Particulate removal from air using filters is required to prevent sorbent mat from plugging.

Sorbent Make-Up Requirements – There are no sorbent make-up requirements for the process. The sorbent is expected to have a lifetime of five years before it needs to be replaced.

Waste Streams Generated – Depleted air stream and condensed liquid water.

Proposed Module Design – Please refer to Figure 2.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	311	—
Cost of Carbon Avoided	\$/tonne CO_2	—	—
Capital Expenditures	\$/tonne CO_2	24	—
Operating Expenditures	\$/tonne CO_2	259	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per tonne of CO_2 captured.

Operating Expenditures – Projected operating expenditures in dollars per tonne of CO_2 captured.

TABLE 3. COST ASSESSMENT OF THE SORBENT TECHNOLOGY

Line	Items	Units	Value
1	Major Equipment (blower, heat exchanger, vacuum pump, and compressors) Cost	$	506,921
2	Projected Lifetime of the Equipment	years	15
3	Major Equipment Annual Costs (= line 1/line 2)	$/year	33,795
4	Utility Costs for Major Equipment (compressor, heater, vacuum)	$/year	776,480
5	Total Major Equipment and Utility (= line 3+line 4)	$/year	810,275
6	CO_2 Capture Rate	tonne/hr	0.3425
7	Major Equipment and Utility Cost Per Tonne CO_2 Produced	$/tonne CO_2	270
8	Cost of PEF Embedded with HNC Sorbent Particles	$/tonne CO_2	13.0
9	Total Capital Costs (total of lines 7 and 8)	$/tonne CO_2	283
10	Total Operating & Maintenance Costs (10% of line 9)	$/tonne CO_2	28.3
11	Total CO_2 Production Costs (total of lines 9 and 10)	$/tonne CO_2	311

Table 3 indicates that the estimated sorbent DAC cost of **$311/tonne** of CO_2 captured is only 44% of Climeworks' sorbent technology (~$700/tonne). Note that the lower cost is mainly due to the high CO_2 adsorption capacity[1,2] of this project's sorbent, as Sholl et al.[3] also reported that the CO_2 capture cost in DAC would decrease by 43–46% when the CO_2 adsorption capacity of the sorbent is doubled. Further analysis indicates this project's CO_2 capture cost could decrease to **$169/tonne** if waste heat is used for desorption instead of electricity. A more comprehensive cost assessment will be performed at the end of the project during the high-level design and analysis based on the experimental data and kinetic parameters collected.

1. Wurzbacher, J. A., Gebald, C., Piatkowski, N. & Steinfeld, A. Concurrent Separation of CO_2 and H_2O from Air by a Temperature-Vacuum Swing Adsorption/Desorption Cycle. *Environ. Sci. Technol.* **46**, 9191–9198 (2012).
2. Wurzbacher, J. A., Gebald, C. & Steinfeld, A. Separation of CO_2 from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. *Energy Environ. Sci.* **4**, 3584–3592 (2011).
3. Kulkarni, A. R. & Sholl, D. S. Analysis of Equilibrium-Based TSA Processes for Direct Capture of CO_2 from Air. *Ind. Eng. Chem. Res.* **51**, 8631–8645 (2012).

Calculations Basis – The operational process (Figure 2) was translated into a compact process design (Figure 5) and modeled in ASPEN using the project team's preliminary experimental data, projected sorbent performance, and literature data for capital cost and energy calculation.[4,5] Three groups of sorbent mats are included in the design, and each group has six steps to finish one cycle.

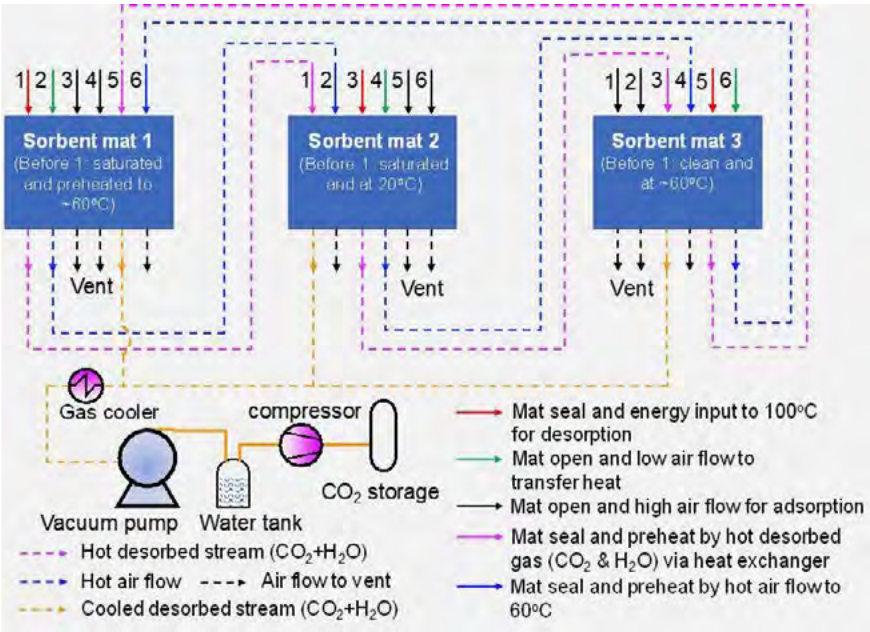


Figure 5: Proposed process flow for DAC.

4. Wurzbacher, J. A., Gebald, C., Brunner, S. & Steinfeld, A. Heat and mass transfer of temperature–vacuum swing desorption for CO_2 capture from air. *Chem. Eng. J.* **283**, 1329–1338 (2016).
5. Peters, M. S. & Timmerhaus, K. D. *Plant design and economics for chemical engineers*. (McGraw-Hill Press, 1991).

Scale of Validation of Technology Used in TEA – The basis for the cost assessments is 3,000 tonnes captured CO_2/year (3,000 tonne/year was selected for this preliminary cost assessment to be compared to published data on the Climeworks technology[4]).

Qualifying Information or Assumptions – In the assessments, the lifetime for the PEF fiber sorbent was assumed to be five years. The other capital equipment was assumed to have a 15-year operating life. The total annual operating and maintenance costs were assumed to be 10% of the total capital costs.

technology advantages

- Small amines with molecular weight less than or equal to 200 g/mol trapped in HNCs enable fast reaction kinetics, high amine efficiency, and high CO_2 sorption capacity for dilute CO_2 (~400 ppm) in the air.
- Thin coating with molecular-sized pores (0.4–0.6 nm pores) effectively prevents small amines from leaking during the heat regeneration process and thus achieving good sorbent stability.
- Innovative macroscopic scaffold with small fiber size (2–5 μm) and porous features allows high sorbent loading and fast and effective exposure of sorbent material to the air.

R&D challenges

- Amine Loading and Sealing: Developing effective amine loading and sealing processes on samples with microporous coating; conducting amine loss evaluation.
- PEFs Loaded with Sorbent: Optimizing electrospinning conditions to incorporate sorbent materials; characterizing composite sorbent structure.

status

SUNY-Buffalo has prepared coated SBA-15 by pore filling and precursor loading via vapor condensation and liquid-phase preparation methods. Microporous coating deposition processes, based on both vapor condensation and liquid filling, were developed; crystal violet (CV) rejection suggested that microporous coatings with pore sizes smaller than 1.3 nm were successfully deposited; and O-xylene uptake indicated less than 0.7-nm coating pores were formed under optimized coating preparation conditions. Further studies are being conducted to modify samples with microporous coating by molecular layer deposition in order to fine-tune the coating pore size, and CO_2 sorption performance evaluation will be conducted on the newly prepared sorbents that are incorporated in PEFs.

available reports/technical papers/presentations

Miao Yu, "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11097&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Hollow+Fibers.pdf*.

Miao Yu, Bin Mu, Shiguang Li "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11099&filename=Direct+Air+Capture+Using+Trapped+Small+Amines+in+Hierarchical+Nanoporous+Capsules+on+Porous+Electrospun+Fibers.pptx*.

Miao Yu, Bin Mu, "Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Hollow Fibers," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Yu.pdf*

TRAPS: Tunable Rapid-Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2

primary project goal

The Palo Alto Research Center Inc. (PARC), in collaboration with Lawrence Livermore National Laboratory (LLNL), is developing a novel solid sorbent for direct air capture (DAC) of carbon dioxide (CO_2). The innovative sorbent, Tunable Rapid-uptake AminoPolymer Aerogel Sorbent (TRAPS) builds on PARC's proprietary polymer aerogel synthesis platform, which will be adapted to produce a polyamine aerogel with a combination of high CO_2 capacity, rapid uptake kinetics, resistance to degradation, and low cost. During the project, PARC is developing the novel TRAPS sorbent and LLNL is testing the performance of the sorbent under DAC-relevant conditions in a lab-scale fixed-bed reactor. TRAPS will yield substantial improvements to process cost, energy consumption, and sorbent lifetime, drastically improving the economic viability of DAC.

technical goals

- PARC will develop a synthesis process to produce polyamine aerogels achieving, at 400 parts per million (ppm) CO_2 in air, high equilibrium CO_2 capacity, rapid uptake rate, and oxidative stability greater than benchmark silica-supported poly(ethylenimine) (PEI).
- PARC will produce sorbent at scales required for fixed-bed performance evaluation and characterize its physical properties to inform the future design of a DAC contactor.
- LLNL will demonstrate the performance of the sorbent under DAC-relevant conditions (400 ppm CO_2) in a lab-scale fixed-bed reactor.
- LLNL will develop a high-level model to assess the performance and cost of a notional DAC process incorporating the sorbent.
- Develop a techno-economic assessment (TEA) to compare against commercial technologies.

technical content

PARC's development of TRAPS solid sorbent for DAC technology will deliver simultaneous advances in all areas identified by the National Academy of Sciences (NAS), with the potential to achieve a disruptive process cost below \$100/tonne CO_2, using estimates from the NAS report. The aerogel structure (Figure 1) that results from PARC's proprietary polymerization process provides numerous benefits to the TRAPS sorbent for DAC applications, including:

1. High equilibrium-loading of CO_2 4 mmol/g due to minimization of inert content in the aerogel.
2. High uptake rate (45-minute full cycle) achieved by controlling aerogel structure through synthesis. High specific surface area combined with high amine incorporation provides a large number of accessible surface sites for sorption. Porosity in the mesopore size regime enables efficient gas transport.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Polyamine Aerogel Sorbent for DAC

participant:
Palo Alto Research Center Inc.

project number:
FE0031951

predecessor projects:
N/A

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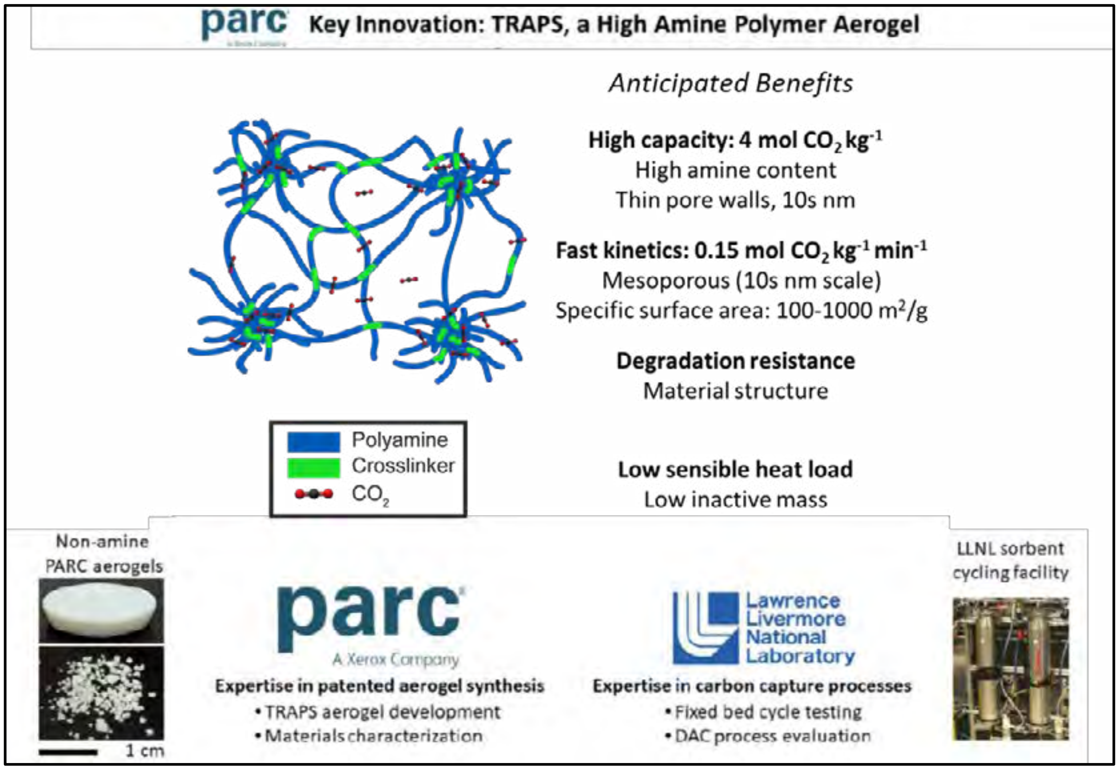
partners:
N/A

start date:
02.16.2021

percent complete:
55%

3. Improvement in oxidative stability over conventional ceramic-supported PEI sorbents is expected due to the covalent integration of amines and control of chemical environment.
4. Low sorbent cost due to use of commodity precursors and scalable processes. In the NAS study, the sorbent budget, \$50/kg, is higher than the expected cost of the sorbent. The expected long-term cost of TRAPS is in line with cost models that use a carbon price of \$100/tonne CO_2.
5. Low minimum sensible heat load due to low content of inert materials.
6. System-integration benefits—the sorbent will be compatible with a variety of schemes for heat integration and regeneration.



parc Key Innovation: TRAPS, a High Amine Polymer Aerogel

Anticipated Benefits

High capacity: 4 mol CO_2 kg^{-1}
High amine content
Thin pore walls, 10s nm

Fast kinetics: 0.15 mol CO_2 kg^{-1} min^{-1}
Mesoporous (10s nm scale)
Specific surface area: 100-1000 m^2/g

Degradation resistance
Material structure

Low sensible heat load
Low inactive mass

Expertise in patented aerogel synthesis
- TRAPS aerogel development
- Materials characterization

Expertise in carbon capture processes
- Fixed bed cycle testing
- DAC process evaluation

Figure 1. TRAPS concept overview.

Sorbents for DAC are deployed in a variety of contactor designs. PARC's polymerization process has been used to produce aerogels in a variety of form factors ranging from 25–100 µm particles to 0.3 x 10 x 10 cm^3 monoliths. TRAPS could be produced as binder-free pellets, fluidizable particles, or cast onto macroporous substrates. Due to the intrinsic toughness of polymers, TRAPS particles are advantaged in crush- and attrition-resistance over brittle ceramic sorbents.

TABLE 1: DAC SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	1000
Bulk Density	kg/m^3	—	450
Average Particle Diameter	mm	—	Controllable
Particle Void Fraction	m^3/m^3	—	0.3
Packing Density	m^2/m^3	—	0.24 x 10^9
Solid Heat Capacity @ STP	kJ/kg-K	—	1.2
Crush Strength	kg_f	—	2
Attrition Index	-	—	0.4
Thermal Conductivity	W/(m-K)	—	0.14
Manufacturing Cost for Sorbent	\$/kg	—	—

Adsorption			
Pressure	bar	—	.0004 CO_2
Temperature	°C	—	25
Equilibrium Loading	g mol CO_2/kg	—	4
Heat of Adsorption	kJ/mol CO_2	—	90-45
CO_2 Adsorption Kinetics	gmol/time	—	0.15 mmolCO_2/g/min
Desorption			
Pressure	bar	—	0.5
Temperature	°C	—	110
Equilibrium CO_2 Loading	g mol CO_2/kg	—	0.4 (remaining)
Heat of Desorption	kJ/mol CO_2	—	90-50
CO_2 Desorption Kinetics	gmol/time	—	0.3 mmolCO_2/g/min

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading. Measured data are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Kinetics – A characterization of the CO_2 adsorption/desorption trend with respect to time, as complete in the range of time as possible.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Atmospheric Air Feed-Gas Assumptions:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
		CO_2	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	°F	0.04	variable	78.09	20.95	0.93	trace	trace

technology advantages

- Enable cost less than \$100/tonne CO_2, leveraging unique pore characteristics to improve lifetime capture capacity of sorbent.
- Significantly lower energy consumption due to reduced sensible heat load.

- Enable cycle life greater than 10,000 by tuning the chemical environment around amine sites in the aerogel.
- High equilibrium loading is achieved by minimizing inert material in the aerogel.
- High uptake rate 45-minute full cycle is achieved by controlling aerogel structure through synthesis.
- Improvement in oxidative stability over conventional ceramic-supported PEI sorbents.
- Low sorbent cost is enabled by using a demonstrated, scalable polymerization process; high-volume, low-cost precursors; and rapid ambient drying of the aerogel.

R&D challenges

- Adapting synthesis to incorporate amine.
- Maximizing amine content without sacrificing pore structure.
- Achieving long cycle life is a challenge for solid sorbents, in general.

status

PARC prepared amine sorbents using the TRAPS aerogel process and explored two classes of post-processing conditions within each downselected post-process condition to maximize amine content and surface area. Physical properties of the sorbents were studied, including preliminary multi-cycle sorbent stability using thermogravimetric analysis. The initial materials exhibit CO_2 uptake at low CO_2 partial pressures. PARC manufactured sorbent material at the ~5-g-scale for packed-bed testing at LLNL; the porosity was robust for pelletization and handling. PARC is currently investigating the impact of surface area on CO_2 adsorption/desorption and understanding the quantitative correlation between process conditions and amine content.

available reports/technical papers/presentations

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11045&filename=TRAPS%3a+Tunable+Rapid+Uptake+AminoPolymer+Aerogel+Sorbent+for+Direct+Air+Capture+of+CO2.pdf*.

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" Project kickoff meeting presentation, Pittsburgh, PA, April 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11043&filename=Tunable+Rapid+Uptake+Amino+Polymer+Aerogel+Sorbent+for+Direct+Air+Capture+of+CO2.pdf*.

Mahati Chintapalli, "TRAPS: Tunable Rapid Uptake AminoPolymer Aerogel Sorbent for Direct Air Capture of CO_2" PARC, A Xerox Company, 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Chintapalli.pdf*

Electrochemically-Driven Carbon Dioxide Separation

primary project goal

The University of Delaware is developing an electrochemically-driven carbon dioxide (CO_2) separator (EDCS) using poly(aryl piperidinium) (PAP) ionomers that performs near-continuous CO_2 separation from air under ambient conditions at a rate of 0.4 mol/m^2-hr with ≤ 235 kJ/mol (1.48 MWh/t) electrical energy input and zero thermal energy input. The novel EDCS process is distinct from thermal separation technologies for direct air capture (DAC) by use of an electrochemical driving force across a membrane to perform both capture and release of CO_2 within a single electrochemical cell.

technical goals

- Fabricate structured membranes with porosity and internal air flow channels to provide high interfacial area for CO_2 uptake and low air pressure drop.
- Characterize dense PAP membranes to determine the fundamental kinetic, thermodynamic, and transport properties as a function of temperature, relative humidity (RH), and degree of carbonation.
- Test porous and structured membranes for through-plane conductivity and volumetric CO_2 mass transfer coefficient.
- Fabricate EDCS cells (25 cm^2) using composite electrodes and a flow-through membrane and test for CO_2 separation over a range of simulated conditions.
- Optimize electrode composition using electrochemical cycling without CO_2.
- Develop an electrochemically driven CO_2 separator with a final performance level of ≥0.4 mol/m^2-hr CO_2 capture rate at 235 kJ/mol CO_2 electricity consumption.
- Characterize PAP properties to support future development.

technical content

The EDCS concept can be applied with different cell configurations and different electrode reactions. The EDCS cell is shown in Figure 1. A pair of nickel hydroxide ($Ni(OH)_2$) electrodes generate a flux of hydroxide (OH^-) anions through a flow-through membrane with air channels. Nickel hydroxide electrodes are used in rechargeable nickel metal hydride (NiMH) and nickel–cadmium (NiCd) batteries. The electrodes are identical and alternate roles as anode and cathode as the cell is cycled, with cycle times of one to four hours. Nickel hydroxide electrodes are durable, with 30,000 cycle lifetimes demonstrated in nickel-hydrogen ($Ni\text{-}H_2$) batteries. Air is blown through the air channels inside the membrane. OH^- passing through the membrane reacts with CO_2 in air to make carbonate (CO_3^{2-}). The membrane is a hydroxide exchange ionomer (HEI) and transports OH^-, CO_3^{2-}, and bicarbonate (HCO_3^-) along a potential gradient. At the anode, consumption of OH^- lowers the pH, decomposing CO_3^{2-} and releasing pure CO_2. Each electrode will produce CO_2 for the half cycle, during which it serves as anode. Although the current is cycled, air follows a single flow path through the membrane, and a pair of check valves at electrode outlets collect CO_2 from anode and prevent backflow to the cathode.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Electrochemical CO_2 Separator for DAC

participant:
University of Delaware

project number:
FE0031955

predecessor projects:
N/A

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partners:
N/A

start date:
10.01.2020

percent complete:
83%

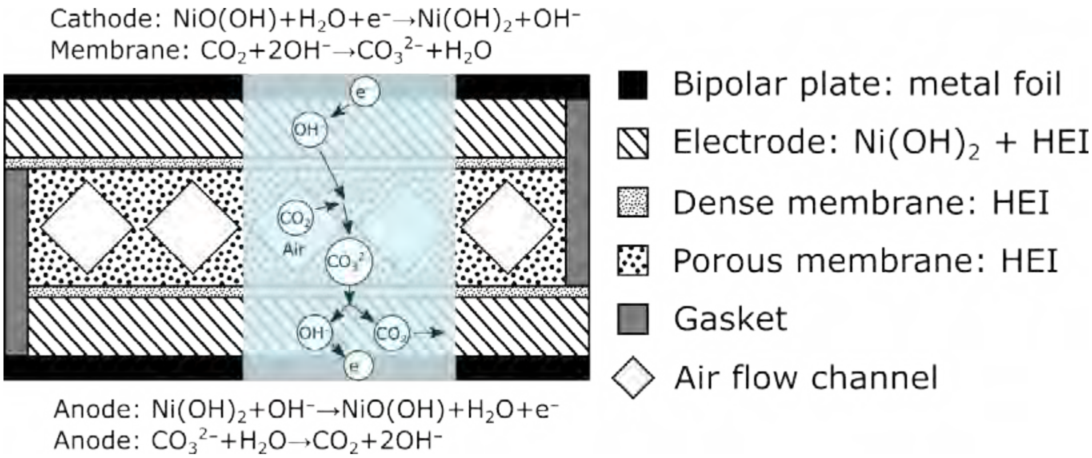

Figure 1: Schematic of EDCS showing the cross section of a single cell.

In Figure 1, air enters through the air flow channels in the membrane. Hydroxide is generated at the cathode by the reduction of nickel oxyhydroxide and electrochemically driven through the membrane. Carbon dioxide reacts with hydroxide to make carbonate. At the anode, the oxidation of $Ni(OH)_2$ causes the pH to drop until decomposition of carbonate occurs, releasing pure CO_2.

The entire process of CO_2 capture, transport, and release in the EDCS occurs under ambient conditions. Dry conditions may require a supply of water to the cathode flow channels for humidification because HEI conductivity depends on water content. However, for a range of RH conditions to be determined in this project, humidification is not necessary and the cell does not consume water.

The project team is focusing on PAP, which was recently developed for fuel cells and electrolyzers and offers very high conductivity, good mechanical properties, and excellent chemical stability. The structure of PAP is shown in Figure 2.

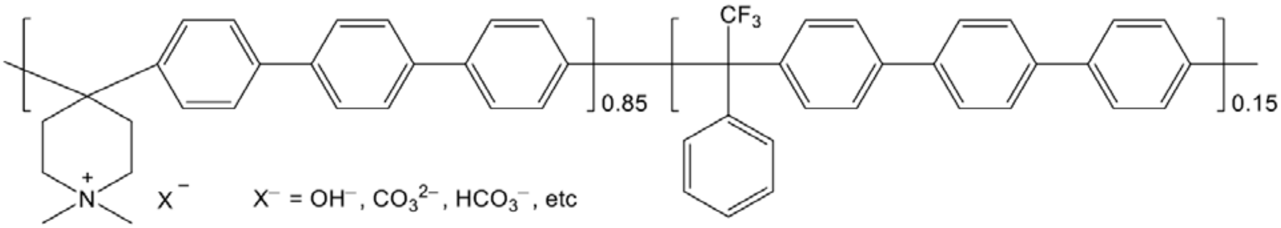

Figure 2: Structure of PAP-TP-x membrane.

A comparison of the EDCS to competing thermal technologies is made in Figure 3. Scenarios A–D show simplified energy balance calculations for amine-based sorbents, using vacuum or steam regeneration. Scenario E shows the aqueous potassium hydroxide (KOH) process piloted by Carbon Engineering, for which a rigorous process analysis has been published. In comparison, the EDCS performance targeted in this project and after more extensive process development and optimization is shown in Scenarios F and G. For vacuum regeneration of amine sorbents, coadsorbed water represents a major issue, as illustrated with Scenarios A–C. Studies have reported $H_2O:CO_2$ ratios of 2.4, 3.9, 5.4, and 7.3 for 20, 40, 60, and 80% RH, respectively. Even in the desert conditions of Las Vegas, Nevada, the annual average RH of 30% corresponds to an $H_2O:CO_2$ ratio of 3.1 and 358 kJ/mol total thermal energy demand. In the steam regeneration scenario (Scenario D), the thermal energy requirement, 169 kJ/mol, is comparable to the most optimistic case. However, Scenario D limited analysis to thermal energy requirement and did not calculate the minimum steam sweep for desorption near 100ºC.

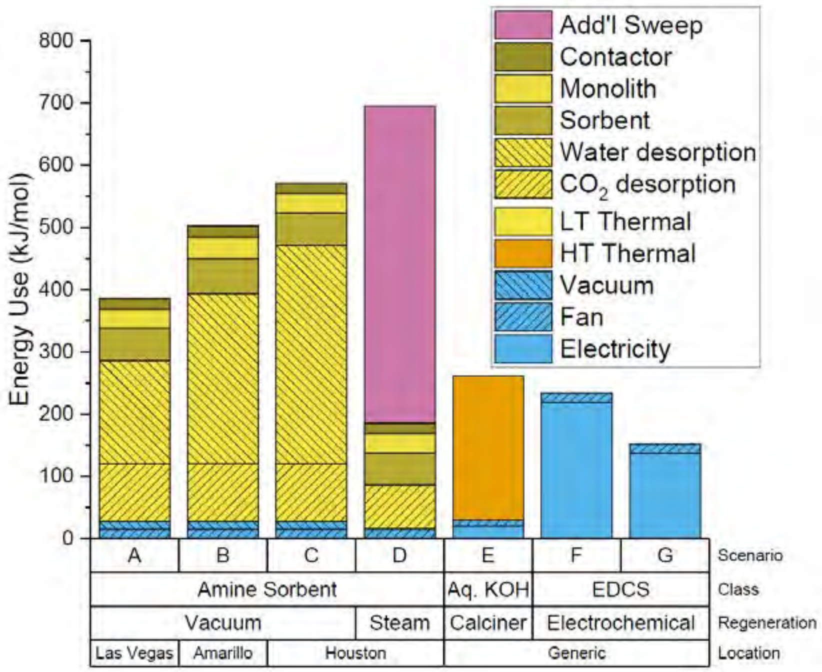

Figure 3: Energy use comparison of DAC technologies.

In Figure 3, Scenarios A, B, and C are based on vacuum desorption of a supported amine sorbent with CO_2 and water desorption energy following the calculations of Wurzbacher et al. Scenario D is steam regeneration of a supported amine sorbent, TRI-PE-MCM-41, as in Kulkarni and Sholl, with the addition of a steam minimum sweep constraint as discussed in the text. Scenario E represents Carbon Engineering's process, net of CO_2 compression. Finally, Scenarios F and G represent the proposed EDCS, with current project and long-term targets, respectively. For Scenarios A–D, location considers average temperature and RH (Las Vegas, Nevada—21°C, 30% RH; Amarillo, Texas—14°C, 57% RH; Houston, Texas—21°C, 70% RH). The sensible heat requirement has been harmonized for a configuration with 2 mmol/g sorbent capacity, 1:1 monolith to sorbent weight ratio, 0.5:1 contactor to sorbent weight ratio, and heat capacities of 1.4, 0.84, and 0.9 kJ/kgºC for sorbent, monolith, and contactor, respectively. Heats of desorption are 80 kJ/mol for CO_2 and 47 kJ/mol for H_2O in Scenarios A, B, and C, and 67.3 kJ/mol for CO_2 in Scenario D. Regeneration is assumed to occur at 95ºC in Scenarios A–D.

EDCS technologies have been reported in the literature for flue gas CO_2 capture. These cells were powered by "oxygen pump" chemistry, with oxygen reduction reaction (ORR) as the source of hydroxide and oxygen evolution reaction (OER) the sink. Two major disadvantages are the slow electrode kinetics, requiring high cell voltage, and the oxygen product of OER, which is mixed with product CO_2. Electrodialysis has been proposed as a technique to regenerate alkaline solvents for DAC. In electrodialysis, acid and alkaline solutions are regenerated from a neutral salt using bipolar membranes to dissociate water into H^+ and OH^-. The cycles vary, but generally, electrodialysis wastes energy by generating strong acid and base solutions and a pH swing of 14 units requiring 0.83 Volts (V). Some cycles have reduced current efficiency and high energy consumption if strong OH^- solutions are generated. In contrast, the EDCS cell uses the solid-state redox couple of $Ni(OH)_2$ and $NiO(OH)$ with favorable kinetics and no gaseous coproducts. While a charge storage electrode must be cycled, increasing process complexity, a new EDCS has been designed where air is fed through flow channels in the membrane and does not need to be redirected as the cell reverses polarity. Hydroxide ion enters from either electrode to capture CO_2, and the product CO_2 is collected from either electrode using check valves to prevent backflow.

technology advantages

- Lower energy consumption.
- Powered by lower-cost renewables.
- No added emissions.
- No flue gas capture.
- Carbon neutral without storage.

- Continuous separation.
- Modular design.

R&D challenges

- Regeneration using vacuum; determination the experimental tradeoff between vacuum and temperature.
- Performance metrics using steam regeneration, co-adsorbed water may increase heat requirement.
- Difficult to generate a large equilibrium swing, which may result in excess sweep steam requirement and implementation of heat-integration strategies.

status

The University of Delaware has improved electro-precipitation of $Ni(OH)_2$ onto nickel foam electrodes and finalized the cell test station. Conductivity tests and pH monitoring have demonstrated a strong relationship between humidity and carbonate ion conductivity through the membrane. Testing of membrane carbonation from hydroxide to bicarbonate at two different temperatures in the CO_2-enriched stream was conducted to extract kinetic and transport parameters for modeling of the process. Continued efforts are focusing upon optimizing the cell performance, scale-up for a stack system, and developing a techno-economic analysis (TEA) for commercialization.

available reports/technical papers/presentations

Brian P. Setzler, Yushan Yan, “Electrochemically-Driven Carbon Dioxide Separation,” Kickoff Meeting Presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11057&filename=Electrochemically-Driven+Carbon+Dioxide+Separation.pdf*.

Brian P. Setzler, “Electrochemically-Driven Carbon Dioxide Separation,” Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11059&filename=Electrochemically-Driven+Carbon+Dioxide+Separation.pdf*.

Yushan Yan, “Electrochemically-Driven Carbon Dioxide Separation,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Yan.pdf*

Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-Fast Direct Air Capture Enabled by Passive Cooling

primary project goal

The State University of New York (SUNY)–Buffalo, in collaboration with Trimeric Corporation, is developing highly porous membrane adsorbents comprising CO_2-philic polymers and self-assembled inorganic nanocages (SINCs) for rapid temperature swing adsorption using electricity-free solar heating and radiative cooling, enabling an economically viable approach for direct air capture (DAC).

technical goals

- Design and prepare membrane adsorbent based on CO_2-philic polymers and SINCs and design operation cycles with solar heating and radiative cooling for CO_2 capture from air.
- Construct and characterize a DAC prototype with the advanced sorbent and electricity-free desorption; demonstrate the 100-hour continuous operation for DAC.
- Complete the TEA using performance data from the sorbent experiments.
- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.

technical content

The project team is developing highly porous membrane adsorbents comprising CO_2-philic polymers and SINCs with a low resistance to airflow and heat transfer for rapid temperature swing adsorption of CO_2 from the air, enabled by electricity-free solar heating and radiative cooling. The core technical activities will combine three key innovations:

1. Highly porous flat-sheet membrane adsorbents contain CO_2-philic amines that can be easily produced using a phase inversion method.
2. CO_2-philic SINCs can be easily dispersed in the polymers with great stability (compared with the metal-organic frameworks [MOFs]).
3. The adsorption and desorption are integrated with solar heating and radiative cooling for rapid continuous operation, in contrast to traditional long-cycle separate operation.

The membrane adsorbents containing amines, polymers, and SINCs can be produced using a one-step industrial process. The porous membranes coupled with porous SINCs offer low resistance for airflow and fast CO_2 sorption/desorption cycles, while the incorporation of the additional amine groups provides high CO_2 sorption capacity.

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Membrane Sorbents with Self-Assembled Inorganic Nanocages for DAC

participant:
State University of New York–Buffalo

project number:
FE0031960

predecessor projects:
N/A

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partners:
Trimeric Corporation

start date:
10.01.2020

percent complete:
83%

Figure 1 shows the integrated membrane adsorbents and cooling technology into a single portable system to realize continuous and rapid CO_2 production. A thin sorbent membrane (e.g., 20–100 µm thick) is continuously rotated by a cylinder. The thin film at the bottom of the cylinder can reach saturation within five minutes (i.e., adsorption [A]) due to the rapid CO_2 and thermal transport within this thin film into the pores. The use of SINCs instead of MOFs enables the active sorbent sites to be highly dispersed and eliminates the need for the pore-to-pore diffusion that limits cycling time in MOFs. The CO_2 will be released at the top side of the cylinder (i.e., the desorption process [D] in the temperature range of 65–100°C), also within five minutes by the heater illuminated by a concentrated solar beam or battery-driven heater during nighttime. The obtained CO_2 may be used for algae culturing or greenhouse or further purification. Afterward, the adsorbents will be cooled by topology-optimized convection and radiative cooling structure to accelerate the cycle and improve the sorption capacity.

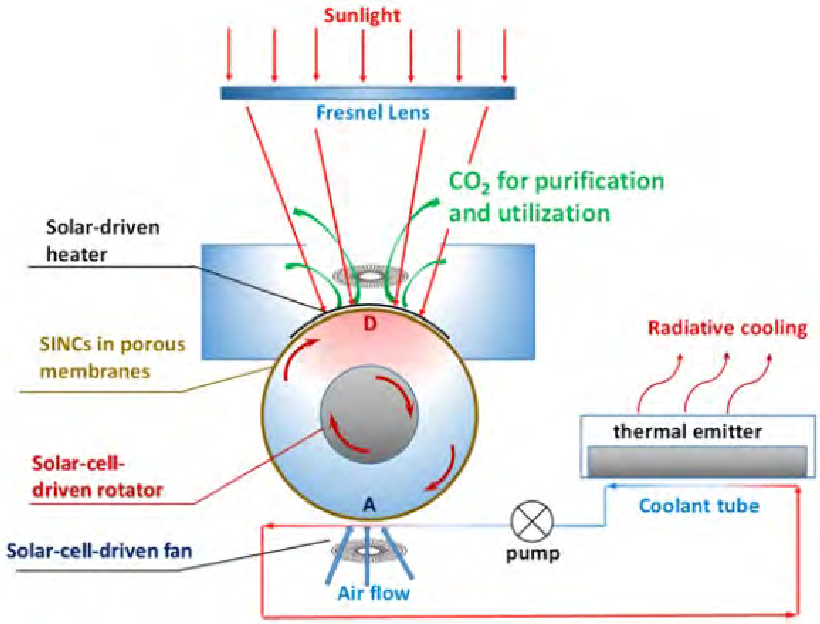

Figure 1: Integrated electricity-free radiative cooling, membrane adsorption, solar heating and desorption, and CO_2 product for further purification and utilization.

One of the key challenges for adsorption, heating, desorption, and cooling of the adsorbents is the time needed for the mass transfer and heat transfer. Ideally, the adsorbents should be embedded in a macroscopic scaffold that effectively exposes them to the air and can be easily heated for desorption. This project proposes a novel sorbent-containing, highly porous, flat-sheet membrane platform (20–100 µm) to decrease the cycle time and thus increase the capacity of CO_2 adsorption. As shown in Figure 2, the porous membranes, with a porosity of 60–95%, can contain CO_2-philic polymers such as polyethylenimine (PEI). Similar to the hollow fiber membranes (HFM)-based adsorbents, these membrane sorbents can be fabricated using existing membrane fabrication equipment and allow for similar CO_2 capture as packed bed systems while significantly reducing pressure drop and accelerating the adsorption and desorption. On the other hand, the flat-sheet platform allows easy packaging into systems with low pressure drop, and the SINCs can be well-dispersed in these highly porous polymers to further reduce mass and heat transfer resistance compared with the MOFs used in the HFM adsorbents.

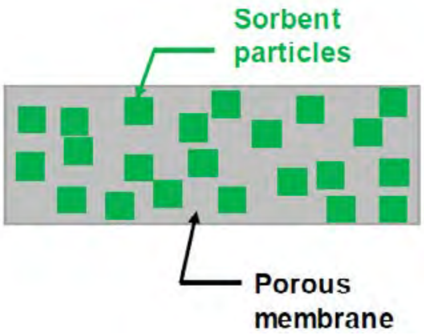

Figure 2: Flat-sheet membrane adsorbents with porosity 60–95% comprising CO_2-philic SINCs and polymers.

Figure 3 shows an example of a sorbent-containing polyvinylidene fluoride (PVDF) membrane developed by SUNY-Buffalo. PVDF membranes can be prepared using phase-inversion processes with pore sizes of 100–1,000 nm and porosity of greater than 90%, as shown in Figure 3a. More importantly, PVDF has high polarity and interactions with SINCs. Figure 3b shows that example SINCs (copper-MOF) are dispersed in the PVDF, and these nanoparticles even decrease the crystallinity of the PVDF, indicating the strong molecular interactions. Physically mixing SINCs with monomer lead to pore filling and blocking, whereas mixing SINCs with solubilized polymer and then casting films, it is possible to maintain porosity. The SINC/polymer integration can also be tailored by functionalizing the SINC ligands with short-chain oligomers to assist with solubilization into the polymer ink and increasing integration without relying on host/guest interactions into the pores.

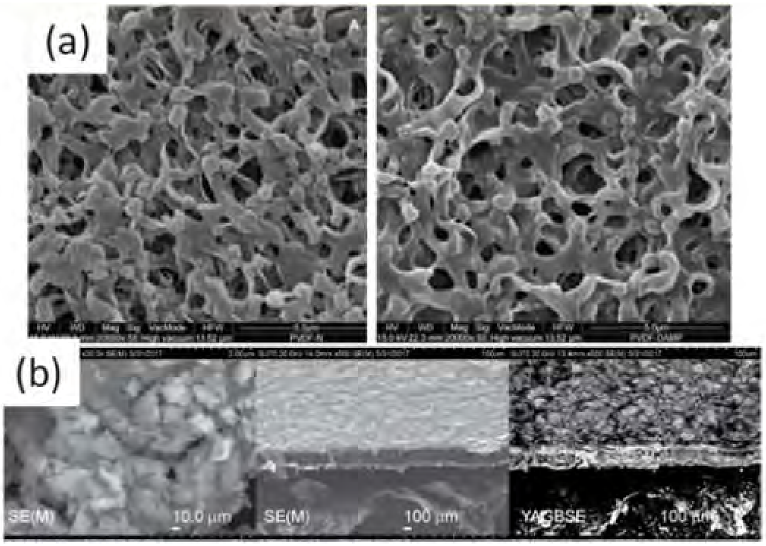

Figure 3: (a) Typical Scanning electron microscopy (SEM) photo of the surface of a porous PVDF membrane, (b) SEM of the hybrid PVDF and example SINCs (copper-MOF).

MOFs are a class of porous materials that have attracted much attention due to their permanent porosity and ability to be tuned at the molecular level through straightforward modular synthetic methods. MOFs are formed by the assembly of metal-containing nodes (metal ions or metal-based clusters) that function as structural building units and organic ligands. Carbon dioxide capture is one of the most active and attractive research areas in MOF applications. The primary challenge of MOF sorbents is their slow adsorption/desorption rate and affinity for CO_2, such that they can capture at the relatively low concentrations found in air. To overcome these challenges, SINCs are proposed as an alternative sorbent, guided by recent successes in the MOF literature. There is a growing library of MOFs that are capable of DAC, and the proposed SINC sorbent materials exploit all of their promising features (high selectivity, high uptake, long-term stability) while reducing adsorption and desorption times to a fraction of those required by frameworks. This reduction is made possible because (i) SINCs obviate the need for air/CO_2 to diffuse throughout large crystallites, and (ii) SINCs are less than 10 nm in diameter and can therefore be incorporated into ultra-thin films that enable innovations to air-capture design, as shown in Figure 4. Even when synthesized as a microcrystalline powders, MOFs range from 150–200 nm, orders of magnitude larger than SINCs. Furthermore, SINCs may be readily functionalized to either enhance mixing into polymers or for covalent incorporation into polySINCs, analogous to recently emerging polyMOFs. The use of ultra-thin porous membranes (i.e., 20–100 µm thick) increases the mass transfer of air to the sorbent sites and decreases the pressure drop, leading to super-fast sorption and desorption and lower energy.

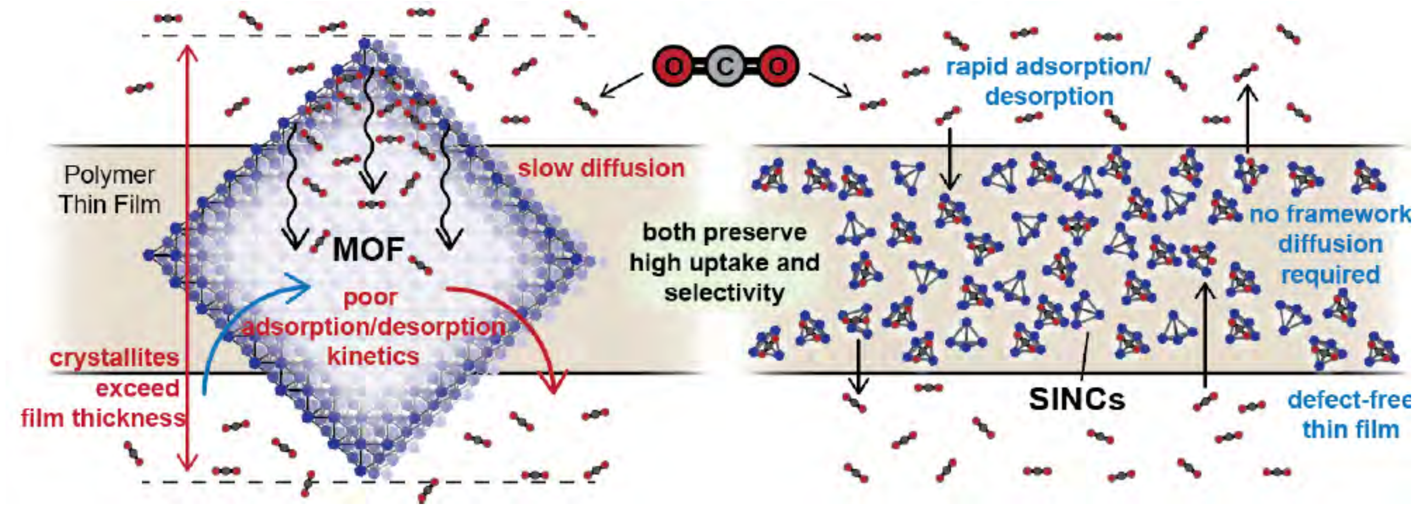

Figure 4: SINC sorbents preserve the high uptake and selectivity of MOFs for DAC while improving upon processability and the kinetics of capture and release of CO_2.

While the solar heating has been widely practiced, daytime radiative cooling has recently emerged as a promising technology to passively cool, even under direct sunlight, by combining a solar reflector with a thermal emitter. The reflector functions in the visible to the near-infrared (IR) spectral region where solar energy is concentrated. It functions as a good thermal emitter in the mid-IR spectral region where room-temperature objects emit most of their radiation energy. Such spectral mismatch is achieved by using nanoscale optical engineering. Recently, SUNY-Buffalo demonstrated electricity-free radiative cooling that operates under direct sunlight. It does not use any energy and yet can provide a cooling power of ~100 Watt/meter^2 (W/m^2) through passive radiative cooling that reaches sub-ambient temperature. It consists of layers of polydimethylsiloxane (PDMS) on an aluminum (Al) substrate with a thickness of 100 µm and 1 mm, respectively. The thermal radiation is primarily emitted by the PDMS layer, which has a near-unity emissivity for wavelengths longer than 4.5 µm due to Si–O and Si–C bond vibrations (Figure 5a), given sufficient film thickness (i.e., larger than 100 µm, as modeled in Figure 5b). Simultaneously, PDMS is transparent to sunlight, which is efficiently reflected by the Al substrate. The resulting emissivity is shown as the red line in Figure 5a.

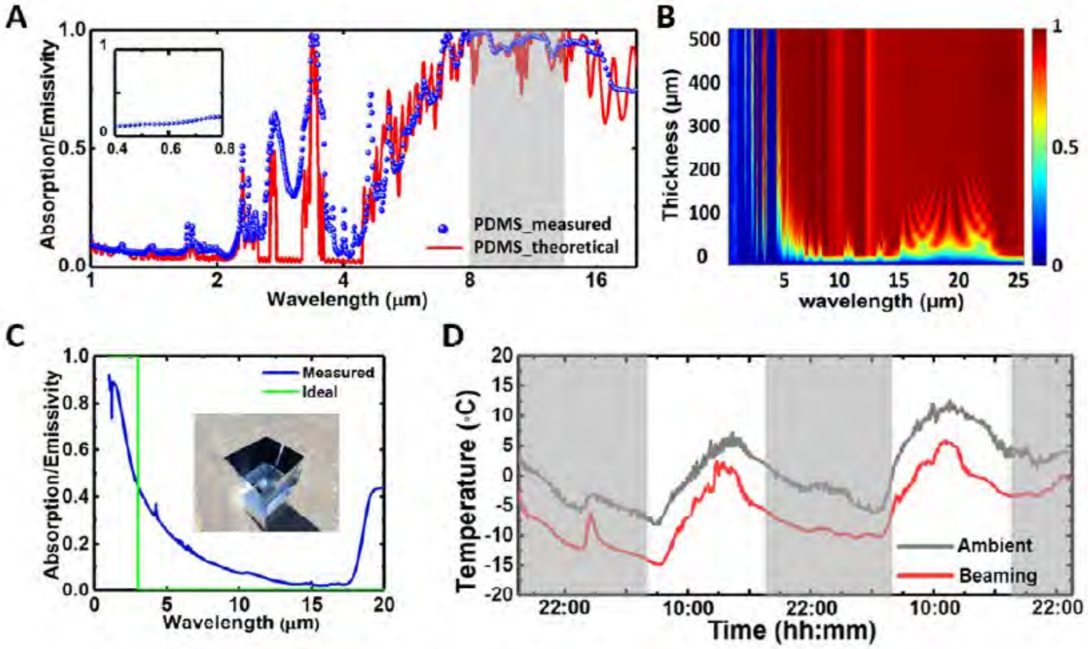

Figure 5: (a) Absorption/emissivity spectra of a planar PDMS/aluminum film with a thickness of 150 µm (solid curve shows numerical modeling and spheres represent measured data); the inset shows that the PDMS film also absorbs part of the solar irradiation in the visible and near-IR regime, (b) the modeled absorption spectra of the planar PDMS/aluminum film as the function of the PDMS film thickness, (c) absorption spectra of an ideal selective absorber (green line) and a commercial spectral selective absorber (blue line), (d) continuous 48-hour cooling test: the grey line indicates the ambient temperature and the red line is the beaming system temperature.

The emissivity of the structure is characterized using Fourier transform infrared (FTIR) spectroscopy. The daytime radiative cooler system reflects almost 96% of the solar radiation (0.3–4 µm) and emits efficiently in the mid-IR region (greater than 4 µm). The radiator was placed inside an insulating box made from polystyrene. A polyethylene film covers the opening of the box to reduce convective heat losses. In addition, a selective solar absorber was used to develop a V-shaped beam-shaping structure to guide the thermal radiation (see the photo in the inset of Figure 5c). Figure 5d compares the temperature of the system (red curve) and the ambient air (grey curve) in 48 hours. This cooler achieves a temperature reduction of about 7°C throughout the day, validating the electricity-free cooling using sunlight.

technology advantages

- Regeneration cycle achieved by solar heating.
- Electricity-free radiative cooling.
- SINCs have been found to increase CO_2 capacity of membrane sorbents.
- SINCs provide permanent pores to increase gas diffusivity and open metal sites to interact with CO_2.

R&D challenges

- Achieving sufficient radiative cooling for this application.
- Carry out radiative cooling and heating outside.

status

Studies have been completed on the influence of the substrate on CO_2 sorption using porous substrates such as fumed silica, SBA-15, gama-alumina, MIL-101(Cr), and Mg_2(dobpdc), where the fumed silica and SBA-15 with 30 wt% polyethyleneimine show the highest CO_2 capacities of 3.0 mmol/g. The SINC membrane with the lowest loading (14–16 wt% amine loading) exhibited the highest amine efficiency. A working prototype of the solar thermal porous membrane DAC sorption system has been designed, assembled, and tested. The membrane adsorbents exhibit CO_2 capacity of ~0.5 mmol CO_2/g at 400 parts per million (ppm) CO_2 in air at 22ºC. Increasing the sorption temperature from 22 to 50°C resulted in 50–100% higher CO_2 capacity and amine efficiency. Work is continuing on the synthesis of high-amine-content SINCs, and to incorporate the most promising SINCs into the membrane sorbent. Evaluation of the effect of humidity on CO_2 capacity is currently being conducted. Scale-up of the conceptual design and the development of a TEA for the pilot process is also in progress.

available reports/technical papers/presentations

Haiqing Lin, Timothy Cook, Qiaoqiang Gan, Andrew Sexton, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11076&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf*.

Haiqing Lin, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," Direct Air Capture Kickoff Meeting Presentation, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11074&filename=Membrane+Adsorbents+Comprising+Self-Assembled+Inorganic+Nanocages+(SINCs)+for+Super-fast+Direct+Air+Capture+Enabled+by+Passive+Cooling.pdf*.

Thien (James) Tran, "Membrane Adsorbents Comprising Self-Assembled Inorganic Nanocages (SINCs) for Super-fast Direct Air Capture Enabled by Passive Cooling," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Lin.pdf*

High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air

primary project goal

InnoSense LLC is developing a direct air capture (DAC) system for carbon dioxide (CO_2) separation from ambient air using a hybrid polymer membrane to reduce CO_2 separation costs and energy penalties. Highly CO_2-selective, ultra-thin, functionalized hybrid polymer membranes (HypoMem), integrated with carbon materials such as graphene oxide (GO), are being designed to improve CO_2 capture performance from ambient or near-ambient conditions, thermal and chemical stability, and ease of processability for scale-up.

technical goals

- Fabricate ultra-thin (<100 nm) robust HypoMem and evaluate its properties and performance to establish selection/acceptance criteria for use in a novel CO_2 separation system.
- Conduct lab-scale CO_2 capture experiments to understand the effects of membrane performance (thickness, permeability, selectivity, etc.) and processing conditions (temperature, pressure, humidity, gas compositions, flow rate, etc.) for process optimization on CO_2 capture capacity.
- Integrate the optimized bench-scale CO_2 capture system in the recipient's lab at InnoSense.

technical content

In current DAC processes, sorbents and solvents are commonly used as CO_2 capture media. The disadvantages of sorbents and solvent systems include the need to build a very large structure, the cost and complexity of regenerative systems, and the loss of moisture in dry environments.

Carbon dioxide separation using membrane technology offers energy efficiency, lower cost and simple operation, and is an environmentally friendly process. Deficiencies of polymer membranes still remain, which include low gas permeability and selectivity, high temperature instability, and low flexibility and robustness. In this project, HypoMem is being utilized to overcome these deficiencies. Improvements to polymer membrane separation properties have been achieved by adding GO into the polymer matrix. Improving CO_2 separation performance using mixed matrix membranes has been demonstrated in prior studies where different levels and concentrations of inexpensive GOs were used to improve CO_2 selectivity of membranes. A variety of HypoMems have been created, embedding GO in polymer matrices, such as polyaniline (PANi), Polybenzimidazole (PBI), and Pebax® MH 1657, to improve CO_2 selectivity.

Figure 1 shows the thin-film liftoff (T-FLO) technique for HypoMem fabrication. Here, the active layer, which determines the membrane properties, is cast separately from the support layer. The support layer determines active layer perm-selectivity and morphology. The physical and chemical properties of the active

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Hybrid Polymer Membrane for DAC

participant:
InnoSense LLC

project number:
FE0031968

predecessor projects:
N/A

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partners:
University of Utah

start date:
01.01.2021

percent complete:
67%

layer can be investigated independently from the entire membrane composite. The T-FLO technique shows potential for scaling the HypoMem for real-world applications.

Carbon Dioxide Permeability and Selectivity of HypoMem: HypoMem has demonstrated potential for high CO_2 permeability (up to 1,279 Barrers with pure CO_2) by controlling polymer and GO content. The addition of GO increased not only the free volume between the polymer chains, but also the stability of the membranes.

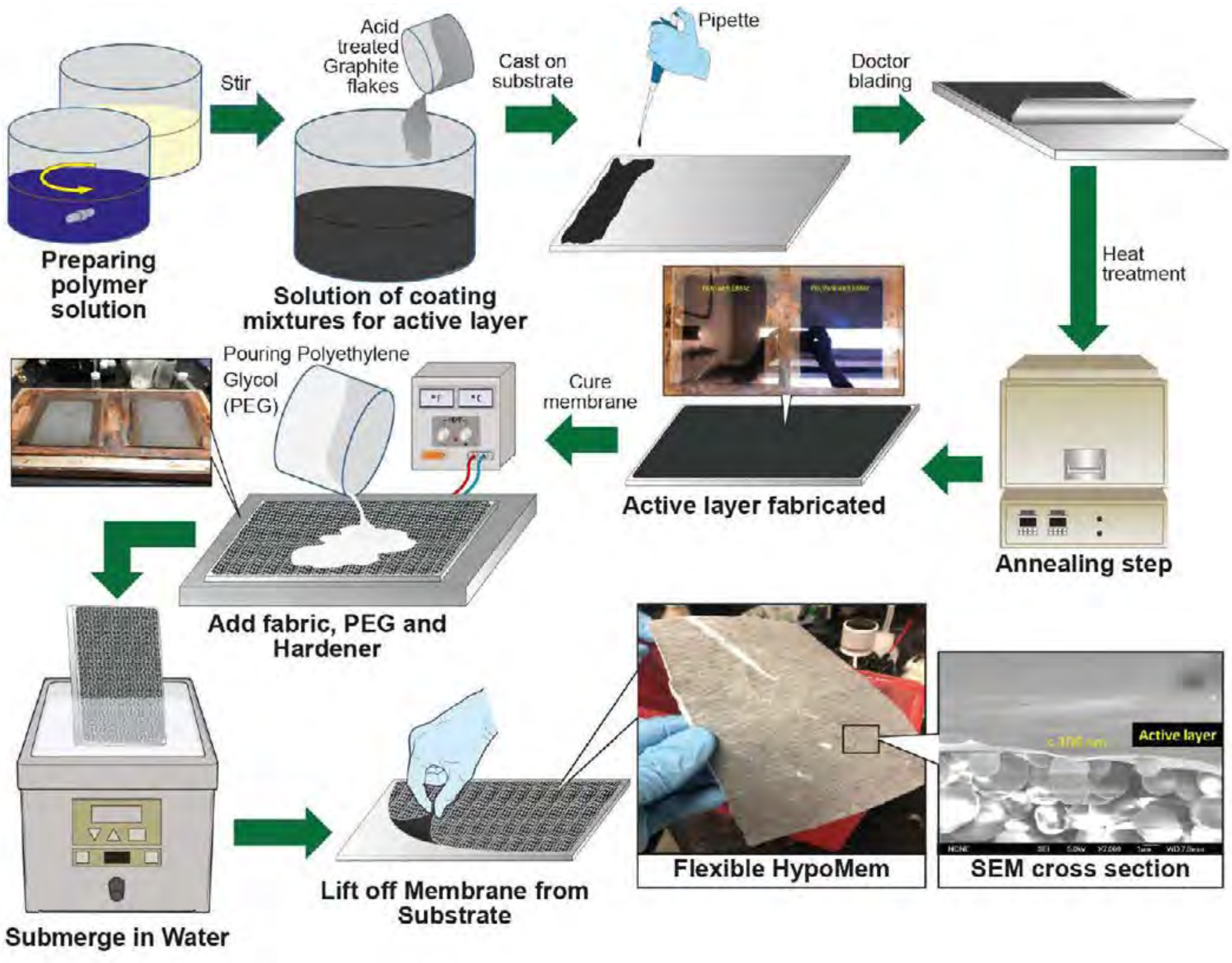

Figure 1: Schematic (follow the arrow from upper left corner) for fabricating HypoMem with functionalized additives.

These morphological changes primarily influence the permeant diffusivity and gas selectivity. The CO_2 permeability and selectivity of HypoMem samples made using the T-FLO technique were demonstrated using pure CO_2 and nitrogen (N_2) gases along with mixtures (15% CO_2, 5% oxygen [O_2], balance N_2) for CO_2 separation tests and compared with other membranes in Figure 2 (A). In earlier work performed, the selectivity and permeability were tuned by employing various polymers and different oxidation levels of carbon materials. Further, HypoMem CO_2 permeability and selectivity were tuned by doping, de-doping, and re-doping with selected acids (e.g., hydrochloric acid [HCl]) and bases (e.g., ammonium hydroxide [NH_4OH]) as reported in literature. HypoMem exhbitis excellent CO_2 separation performance, and is also flexible and mechanically robust. In this project, HypoMem is being formed into spiral-wound configurations for an alpha demonstration. The transport and separation in membranes involves molecular-scale interactions of the permeating gas component with the active layer. More importantly, the extremely thin and defect-free active layer requires a highly porous non-selective support layer. Also, permeability is a pressure- and thickness-normalized flux of a desired gas component. Figure 2 (B) presents the effect of active layer thickness on CO_2 permeability and selectivity in earlier studies. Since the pore size of both the fabric and epoxy layers can be controlled with the T-FLO technique, the molecular transport mechanism can be optimized to further develop HypoMems.

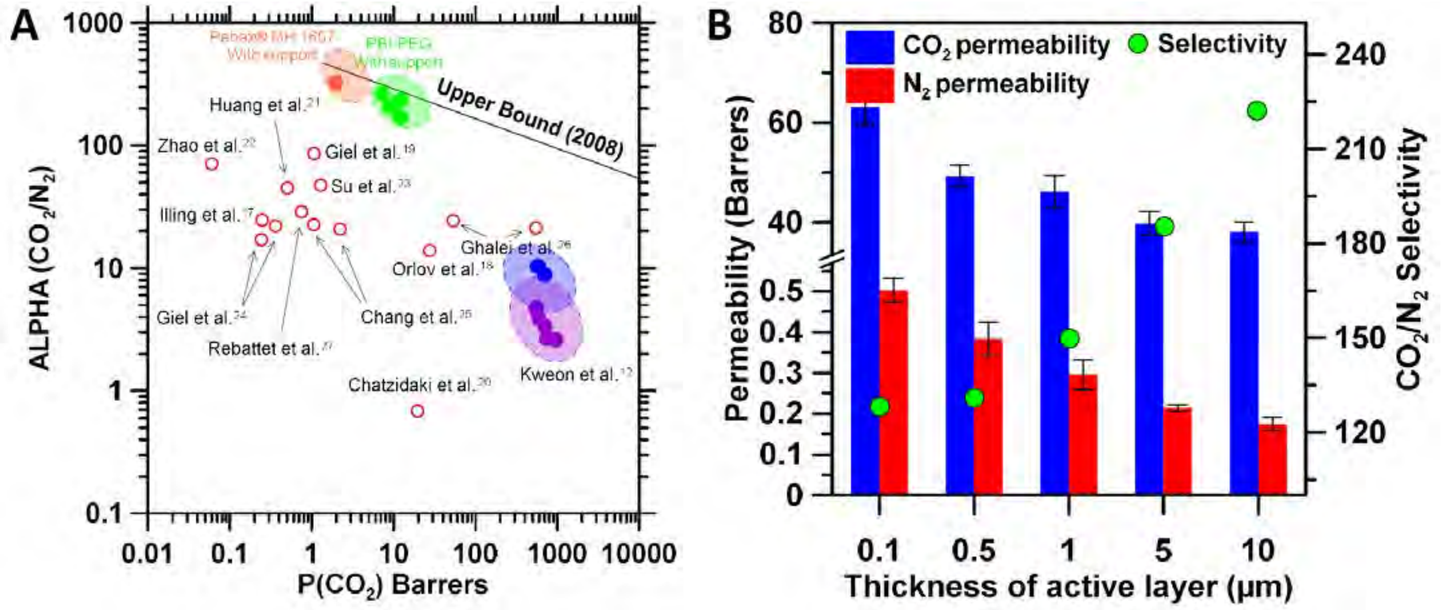

Figure 2: (A) A Robeson plot comparing the performance of the developed HypoMem against other polymer composite membranes for CO_2/N_2 gas separations. (B) Permeability and ideal selectivity data for different thicknesses of active layers with pure CO_2 and N_2.

For gas molecules (e.g., CO_2, N_2, and O_2) smaller than 4 Å, HypoMem combined with functionalized GOs improves gas transport properties with thermal and chemical stability since the gaps of individual GO sheets are slightly bigger than feed gas molecules. Functional groups such as amine and ethylene oxide attached on the active layers have a strong affinity to CO_2 molecules in the presence of N_2 and O_2. However, freestanding polymer membranes tend to crystallize, swell, and break, especially at high water content. To overcome this limitation, different molecular weights of polyethylene glycol (PEG), diglycidyl resin, and diamine hardener have been used in the T-FLO technique. Therefore, in the current scenario, by adding support layer separately, more stable membranes can be generated without changing properties of the active layer. Different molecular weight PEGs are now being employed to control the permeability of crosslinked networks in the support layer. These membranes rely on reversible chemical reactions between the target CO_2 gas and specific functional groups attached to the polymer matrix. Therefore, only the reacting species (CO_2) are transported across the membrane by this mechanism, theoretically increasing both permeability and selectivity. Amines are able to bind CO_2 selectively through different possible chemical mechanisms, such as those shown in Figure 3. The membranes contain amine groups that are considered a convenient medium to selectively transport CO_2 in the presence of humidity. Another important parameter to consider is pH, as it influences amine protonation equilibrium, which in turn affects CO_2 interaction with the active layers. Thus, to exploit the facilitated transport mechanism presented, a neutral amine form is needed to maintain high pH values during material purification and membrane preparation.

Cycle and Operating Conditions: Figure 4 is an overall process schematic of the HypoMem system. First, an ultra-thin active layer is fabricated individually, and then support layers are added to form mechanically robust HypoMem (Figure 4 [2]). Next, HypoMem is formed and packed into the spiral-wound membrane module. If necessary, use of a hollow-fiber module will be examined (Figure 4 [3]). Then, the CO_2 separation system is sealed, and simulated air is injected, passing first through a gas pre-conditioning unit to control humidity and temperature (Figure 4 [1]). Following CO_2 separation, the permeate gas (high-purity CO_2) and rejected gases (N_2, O_2, sulfur dioxide [SO_X], nitrogen dioxide [NO_X], etc.) are collected and exhausted safely (Figure 4 [4]), and, if necessary, additional post treatments can be added. Following a sufficient duration of simulated air injection (one day ≤ t ≤ 30 days), the membrane modules are characterized for any performance degradation.

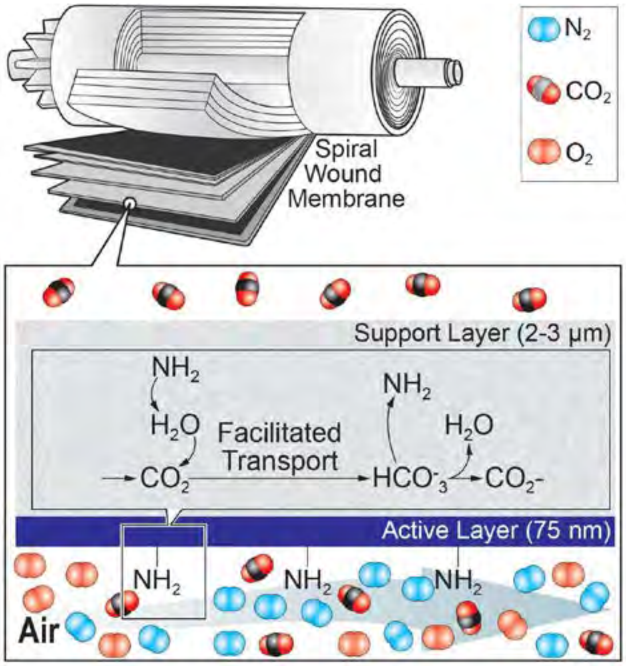

Figure 3: Schematic of facilitated transport mechanism for CO_2 separation from ambient air.

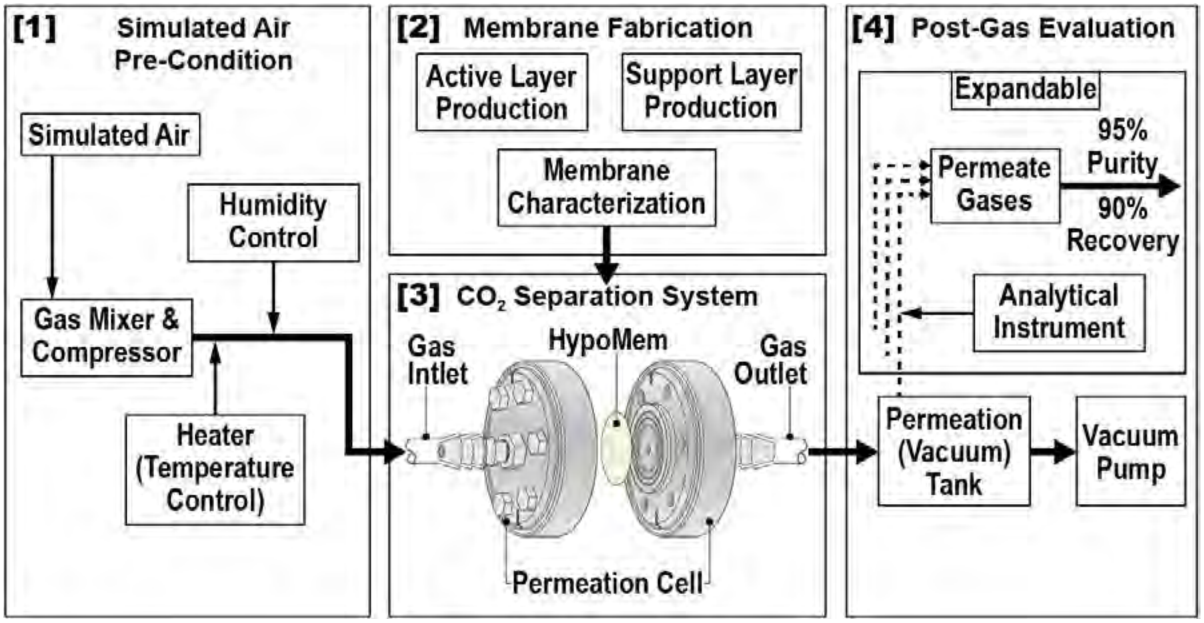

Figure 4: An illustration of the HypoMem CO_2 separation system.

Also, in an earlier study, a multi-stage membrane separation process was considered to improve CO_2 purity and energy efficiency. Final CO_2 purity obtained was 82.1% with 90.7% overall recovery with the use of three stages.

Different compositions of ultra-thin robust HypoMem are a pioneering approach to a cost-effective process for CO_2 separation from a low concentration of CO_2. Through active and support layer modification and chemical treatments, (doping, de-doping, and re-doping), the CO_2 permeability and selectivity can be tuned as needed. The CO_2 separation system's robustness has been demonstrated in terms of CO_2 permeability and selectivity with CO_2 and N_2 mixed gases, and the impact of active layer modification and thickness control on mass transfer resistance has been revealed. Because membrane gas separation is pressure-driven, the thickness of the active layer is the key to maximizing the permeation rate. Using the T-FLO technique, a high-permeance membrane is being fabricated with processability that enables scale-up for commercial applications.

technology advantages

- Material formulations featuring ultra-thin and chemically stable membranes for CO_2 separation.
- T-FLO technique enables controllable pore size fabrication and thickness, enabling improved performance of the active membrane layer.
- Efficient and scalable CO_2 separation system.
- High-permeance membrane that is scalable for commercial applications.
- Mechanically, chemically, and thermally stable membranes reduce costs since the feed streams would not require pretreatment.
- Development of spiral-wound modules and parallel membranes allows for maximum packing density with lower pressure tolerances, enabling maximum CO_2 separation and minimum energy use.

R&D challenges

- Optimizing permeance, permeability, and CO_2 selectivity performance.

status

InnoSense LLC has formulated and fabricated hybrid polymer HypoMem samples with reasonably large size (~8x12 cm) and have verified consistent thicknesses and morphologies of both active polymer layer and epoxy support layers. Researchers have also constructed an onsite gas permeation testing apparatus and observed higher permeance values: 6.83×10^5 gas permeation unit (GPU) for CO_2 and 2.15×10^5 GPU for N_2 at a pressure drop across the membrane of 70 cm of mercury (~95 kPa). The CO_2 selectivity was observed to be 3.17 at permeance of 6,830 GPU. The trend of an increase in CO_2 selectivity corresponded to a decrease in permeability. Computer simulations suggest a multi-stage process is needed to achieve the desired CO_2 permeate concentration for successful DAC CO_2 separation.

available reports/technical papers/presentations

Maksudul M. Alam, "High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11095&filename=High-Performance%2c+Hybrid+Polymer+Membrane+for+Carbon+Dioxide+Separation+from+Ambient+Air.pdf*.

Maksudul M. Alam, Adrien Hosking, Milind Deo, "Development of Hybrid Polymer Membranes for Direct Air Capture of Carbon Dioxide," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Alam.pdf*

Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER) is developing an enhanced depolarized electro-membrane system (EDEMS) for direct air capture (DAC). The EDEMS consists of a low-pressure ceramic membrane contactor/absorber in a tailored electrochemical process that leverages depolarization to regenerate and concentrate both a capture solvent and carbon dioxide (CO_2) extracted by the membrane. The technical objectives of this laboratory-scale project include developing and evaluating patterned ceramic membrane absorbers and a depolarized electrochemical cell (DEC), integrating the components into a novel EDEMS, and conducting continuous operation of the system for DAC.

technical goals

Develop a capture technology to extract CO_2 from atmosphere that reduces the cost of capture through:

- Developing and screening membrane-based contact absorbers to capture ambient CO_2.
- Developing an electrochemical process to regenerate the capture solvent and up-concentrate captured CO_2 at low power requirement.
- Demonstrating stability and performance of absorber for greater than 24 hours with less than 5% reduction in CO_2 flux by leveraging the regeneration capability of ceramic membrane contactor.

technical content

The EDEMS DAC technology streamlines the energy input and reduces the number of unit operations necessary for removing low-concentration CO_2. This process intensifies CO_2 capture using surface patterned ceramic membranes and solvent regeneration via depolarization in electrochemical cells that leverage previously developed UK CAER electrode stabilization techniques.

The separation of CO_2 from other gasses is an important component of many industrial processes, including ammonia production, steel manufacturing, and power generation. Unlike these industrial processes with point source CO_2, a key challenge with DAC is the low concentration of open-source CO_2, approximately 400 parts per million (ppm), requiring large volumes of air to be treated per mole of CO_2 extracted. Consequently, materials with strong CO_2 binding are required for its extraction, limiting sorbent options to mostly alkalines and amines. Figure 1 shows a benchmark DAC process where potassium hydroxide (KOH) removes CO_2 as carbonate via an exothermic reaction ($\Delta H = -63.5$ kJ/mol). Using a membrane contactor, instead of a packed-bed or spray tower absorber, allows for low-pressure operation and provides better process control while avoiding column

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Novel Concepts

project focus:
Enhanced Depolarized Electro-Membrane System for DAC

participant:
University of Kentucky Center for Applied Energy Research

project number:
FE0031962

predecessor projects:
N/A

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partners:
University of Kentucky; ALL4 Inc.

start date:
10.01.2020

percent complete:
80%

flooding issues. However, the regeneration of CO_2 and the capture solvent requires several intensive unit operations, including (1) causticization to convert soluble K_2CO_3 to less soluble $CaCO_3$ and regenerate KOH, (2) clarification to dewater $CaCO_3$ and air separation to provide an oxygenated environment to a calcination step, (3) calcination at high temperatures to extract and release concentrated CO_2, and (4) finally slaking by recombining CaO with water to form $Ca(OH)_2$ to restart the causticization process. The calcination process is the most energy-intensive of the regeneration steps (ΔH = 179.2 kJ/mol), and it also leads to significant water loss via evaporation from the process. A DAC system based on this methodology can cost as much as $2,200/tonne CO_2 per year, which is more than 10 times the cost for post-combustion CO_2 capture. To address the challenges associated with the benchmark DAC process, UK CAER proposes an EDEMS (Figure 2) for the removal of CO_2 from ambient air with an intensified process that significantly reduces the number of unit operations and results in greater than 30% reduction in energy cost to capture and concentrate CO_2 and regenerate the capture solvent by leveraging chemical energy from depolarization.

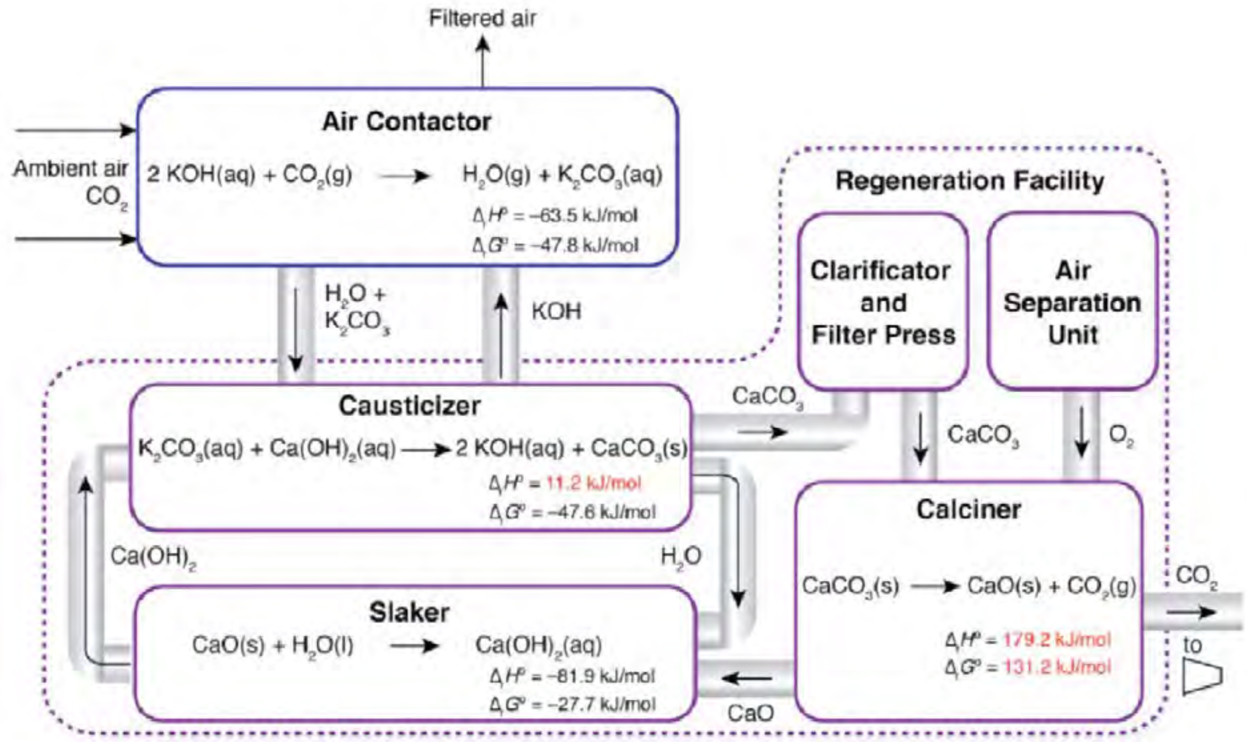

Figure 1: Solvent-based direct air capture system.

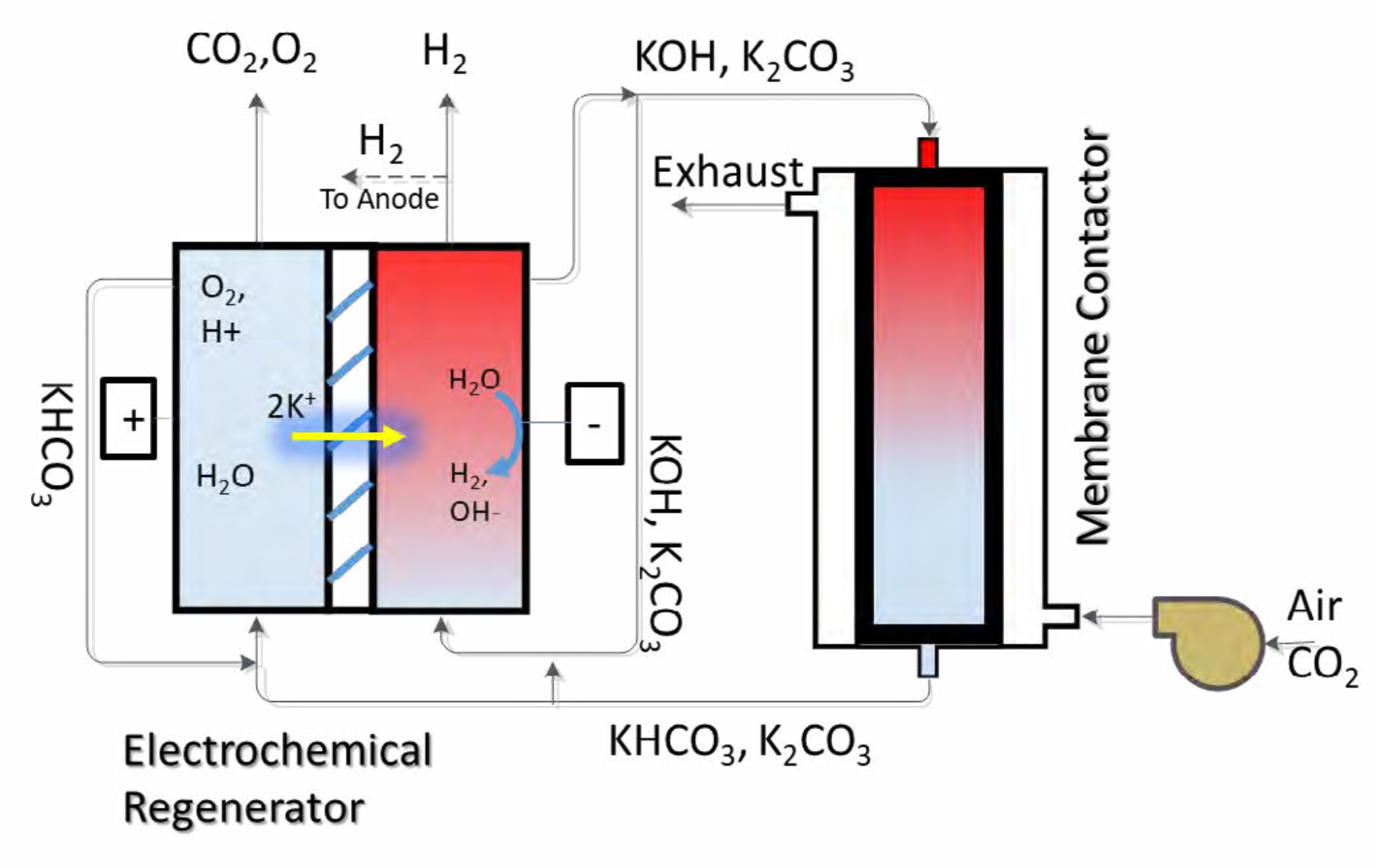

Figure 2: University of Kentucky enhanced depolarized electro-membrane system.

The UK CAER process is composed of (1) a surface-structured enhanced and entirely solvent-compatible ceramic membrane contactor with regenerative wetted surface characteristics, and (2) an advanced DEC unit with in situ production of hydroxides (KOH, NaOH, etc.) for CO_2 scrubbing in the contactor.

The UK CAER contactor/absorber features α-alumina-type ceramic membranes with superhydrophobic layer and greater than two times expanded surface (compared to a pristine membrane) where influent ambient CO_2 is absorbed into KOH through the membrane. The UK CAER contactor, which can increase packing density by more than 50% compared to typical ceramic contactors due to the larger area density provided by its patterned interface, is also chemically stable. Polymeric hollow fiber membranes are also difficult to regenerate following surface wetting and loss of hydrophobicity, while the performance of the UK CAER contactor membranes may be preserved by regenerating the wetted surface at greater than 50°C. Following DAC, K_2CO_3/$KHCO_3$ from the membrane is fed to the DEC to liberate concentrated CO_2. Under normal operation, water splitting with the hydrogen evolution reaction (HER; $2H_2O$ + electrons = H_2 + $2OH^-$) and oxygen evolution reaction (OER; $2H_2O$ = O_2 + $4H^+$ + electrons), are the dominant cathode and anode reactions. The hydrogen produced can be sold to offset some of the capture cost, facilitate energy storage, or depolarize the DEC, leading to lower energy requirement. The DEC leverages depolarization by using H_2 (from HER) for the hydrogen oxidation reaction (HOR, H_2 = $2H^+$ + electrons) in place of the OER at the anode. The depolarization reduces the overpotential (i.e., potential difference required to drive current) by more than 50%, primarily due to its chemical potential contributions. The K_2CO_3/$KHCO_3$ from the contactor is fed to the anode side (some to the cathode as electrolyte), K^+ ions are transported via a cation exchange membrane (e.g., Neosepta CMX or Nafion) to the cathode to combine with OH^-, while CO_3^{2-} or HCO_3^- is converted to CO_2 by reacting with protons produced at the anode.

The UK CAER EDEMS process (Figure 2) can improve on the benchmark processes by:

1. Minimizing the footprint of the treatment process by intensifying the capture and regeneration into two unit operations, avoiding the need for seven units to facilitate cyclical operation.
2. Reducing the need for make-up water, as no thermal evaporation occurs.
3. Avoiding the need for large thermal input and providing a cost-effective process.
4. Generating hydrogen for sale.

5. Seamless compatibility with renewable direct-current electrical power sources, such as solar cells, for stand-alone remote operation.

In addition, by combining the anode and cathode depolarization using a staging approach, voltage requirements may be further reduced.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Material Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Hydrophobic Layer	—	Fluoroalkylsilane	
Materials of Fabrication for Support Layer	—	Alumina	
Nominal Thickness of Hydrophobic Layer	µm	N/A	N/A
Membrane Geometry	—	Tubular	Tubular
Hours Tested without Significant Degradation	hrs	100	100
Membrane Performance			
Temperature	°C	21	21
CO_2 Pressure Normalized Flux	GPU or equivalent	64	90
CO_2/H_2O Selectivity	—	N/A	N/A
CO_2/N_2 Selectivity	—	N/A	N/A
Type of Measurement (ideal or mixed gas)	—	Real Air	Real Air
Capture Fluid		2 wt% KOH, countercurrent	
Regeneration Voltage	V	3.5	2.7

Definitions:

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Shell-Side Fluid – Capture solvent.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

		Composition						
		vol%					ppmv	
Pressure	**Temperature**	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	68-72°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Membrane Permeation Mechanism – The driving force for permeation is partial pressure difference between the gas and liquid sides of the membrane. The electrochemical cell regenerates the solvent after CO_2 is absorbed into the liquid.

Gas Pretreatment Requirements – No treatment of influent air is required.

Product Streams Generated – Hydrogen is generated from the process for sale, energy storage, or depolarization to reduce the energy requirement for capture solvent regeneration.

technology advantages

- Provides stable performance facilitated by the DEC and hydrophobic contact absorber.
- Reduces the energy requirement by up to 30% through intensifying the electrochemical and CO_2 release reactions.
- Provides easy integration with renewable power sources for remote operation and reducing carbon emissions.

R&D challenges for state-of-the-art

- Low CO_2 concentration requires facile capture solvent due to low driving force.
- Regeneration step is energy-intensive.
- Water make-up requirement is high.
- Air separation unit introduces additional cost.

status

Contactor preparation, stability, and performance testing were conducted. Tubular membranes treated with fluoroalkylsilane achieved greater than 90% CO_2 capture using laser-patterned ceramic membrane contactor bundle and a performance similar to polymeric membranes. Electrode design and preparation were conducted for electrochemical regeneration of the capture solvent. The platinum-based catalyst was chosen for depolarized operation. Process integration matching regenerator and contactor performance for continuous operation is continuing, including exploring new configurations for more efficient capture.

available reports/technical papers/presentations

Ayo Omosebi, “Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air,” Project Kickoff meeting, Pittsburgh, PA, November 2020. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11082&filename=Enhanced+Depolarized+Electro-Membrane+System+(EDEMS)+for+Direct+Capture+of+Carbon+Dioxide+from+Ambient+Air.pdf*.

Ayo Omosebi, “Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air,” Direct Air Capture Kickoff meeting, Pittsburgh, PA, February 2021. *https://netl.doe.gov/sites/default/files/netl-file/21DAC_Omosebi.pdf*.

Ayo Omosebi, “Enhanced Depolarized Electro-Membrane System (EDEMS) for Direct Capture of Carbon Dioxide from Ambient Air,” NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Omosebi.pdf*.

Assessment of the Potential for the Decarbonization of Natural Gas with RNG and Bioenergy with Carbon Capture and Storage

primary project goal

Oak Ridge National Laboratory (ORNL), in collaboration with the National Energy Technology Laboratory (NETL) and the Advanced Research Projects Agency–Energy (ARPA-E), is conducting an economics survey for the decarbonization of natural gas. Renewable natural gas (RNG) is a high-methane gas mixture derived from renewable biomass. RNG can be produced via a gasification or anaerobic digestion ("bio-gasification") process, followed by the methanation of syngas (a synthetic natural gas [SNG] process]). When combined with carbon capture and storage (CCS), the overall process can achieve net-zero or even net-negative carbon emissions. The objective of this study is to determine the economics of such a scheme, the point at which the life cycle emissions of such a strategy become zero, and whether or not the costs of such a scheme can compete with traditional natural gas production processes.

technical goals

- Identify a variety of potential sites for an RNG-CCS plant.
- Determine the availability of local biomass at each potential site.
- Perform a life cycle analysis (LCA) to determine carbon avoidance levels and perform a techno-economic analysis (TEA) to determine cost of avoidance.
- Develop marginal carbon avoidance cost (MCAC) curves for each location.
- Perform a sensitivity analysis for each case with respect to multiple process parameters.

technical content

The project begins with a comprehensive geologic and preliminary economics survey of more than 200 locations throughout the United States. Key fundamentals for a successful plant site have been identified as large demand for natural gas, access to existing natural gas infrastructure, and existing carbon dioxide (CO_2) transport and storage (saline reservoirs) infrastructure. Other factors to be considered include available biomass tonnage and diversity, local materials costs, and local competition from other resources. An example of a potential site in Houston, Texas is shown in Figure 1. Sites with at least five terrestrial biomass sources are being selected from this survey. A similar approach is being undertaken by ARPA-E for macroalgae biomass. The sites are being identified using the Oak Ridge Siting Analysis for Power Generation Expansion (OR-SAGE) software tool. OR-SAGE is a spatially explicit biorefinery siting model that runs as a raster analysis, excluding areas that do not meet specified criteria.

According to the 2016 Billion-Ton Report, biomass availability across the continental United States is high, and a diverse array of bioenergy resources is

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Biomass Carbon Removal and Storage

key technology:
Novel Concepts

project focus:
Economics Survey of Biomass-to-Natural Gas Processes with CCS

participant:
Oak Ridge National Laboratory

project number:
FWP-FEAA422

NETL project manager:
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principal investigator:
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partners:
NETL; ARPA-E

start date:
10/01/2021

percent complete:
98%

available, as shown in Figure 2, including municipal solid wastes (MSWs), agricultural waste/residues, woody/forest biomass, and crops. This particular study also includes "wet" biomass, such as macroalgae. In total, the survey includes the following types of specific biomass species for the LCA and TEA: logging residue, whole trees, herbaceous energy crops (switchgrass), crop residues (corn stover), wastes (MSW, construction and demolition [C&D] wastes, and manure), fossil natural gas, macroalgae, and sorghum.

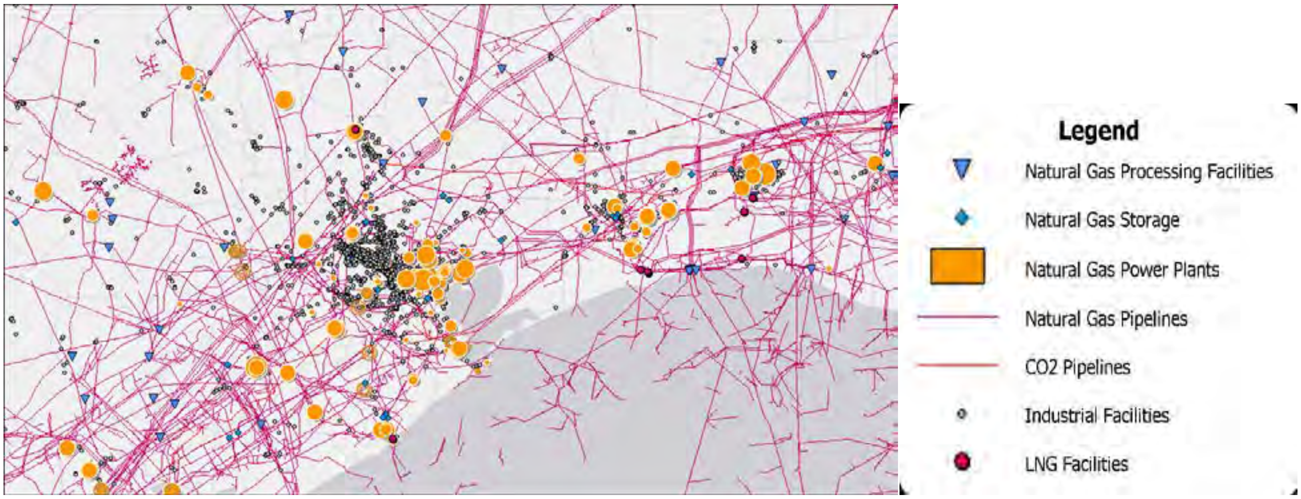

Figure 1: Sample survey location—Houston, Texas.

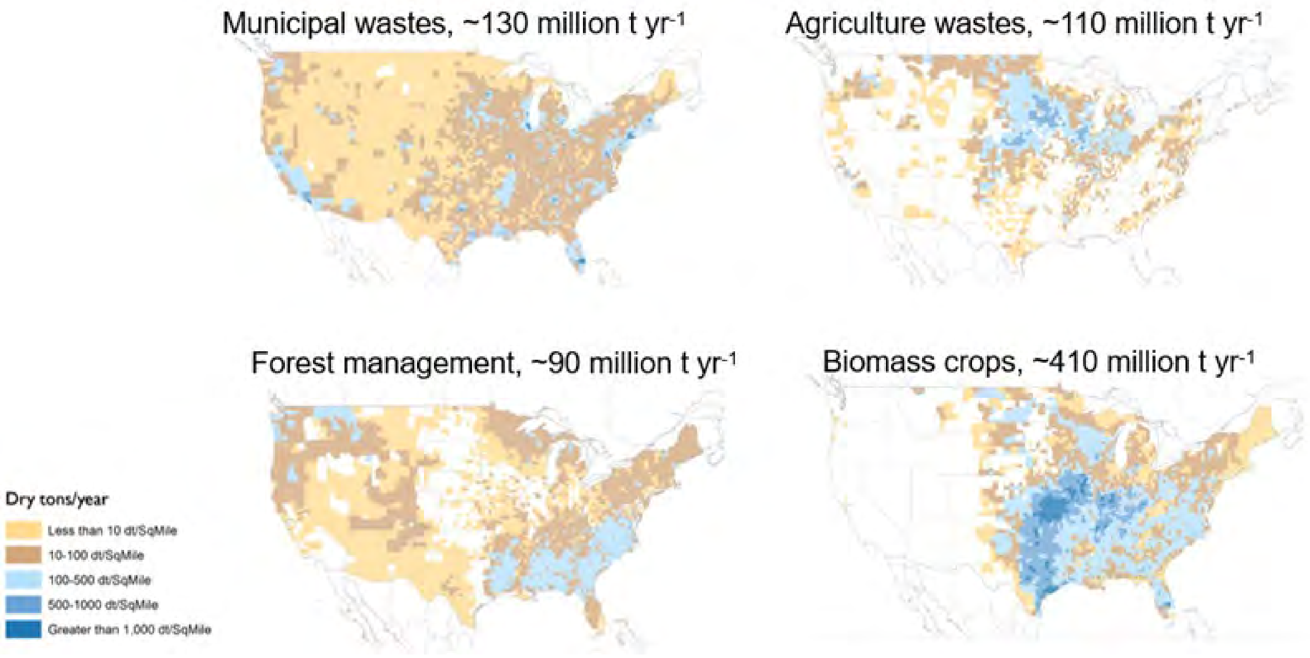

Figure 2: Biomass availabilities at $60/short ton.

ORNL is managing feedstock and site selection and analysis, as well as surveying the available conversion processes up to the point the natural gas is transported to its end-use. NETL is handling the RNG logistics for upgrading, CCS, natural gas end-use, and pipeline access, as well as being chiefly responsible for the final TEA and LCA. Finally, ARPA-E is responsible for all data for macroalgae and anaerobic digestion. The end-use for the produced RNG will explicitly be an optimized natural gas combined cycle (NGCC) plant. The baseline plant with no installed CCS serves as the baseline for all cases, which is then be compared to two CCS schemes—those being 90% and 97% capture. The complete scenario matrix for each of the parameters is given in Figure 3.

TABLE 1: MATRIX OF PARAMETERS SELECTED FOR ALL SCENARIOS

Feedstocks (ORNL/ARPA-E)	Conversion Processes (ORNL/ARPA-E)	Pipeline Transport (NETL/ORNL)	Power Production (NETL/ORNL)	CCS (NETL)
Wastes	Gasification	Natural Gas	NGCC	LCA
Ag. Residues	Pyrolysis	CO_2 (+storage)	NGCC w/ 90% CCS	TEA
Forestland Resources	Anaerobic Digestion		NGCC w/ 97% CCS	Systems/Markets
Energy Crops	CO_2 Storage Basins			
Macroalgae				

technology advantages

- Modeling of biomass resources for decarbonization.
- Quantification of carbon avoidance cost across multiple feedstock-conversion-end-use pathways.

R&D challenges

- Determining optimal site for each type of facility and facility size.
- Completing the LCA and TEA in a timely manner.
- Acquiring the necessary cost and carbon-efficiency data.

status

The project was completed on April 30, 2022.

available reports/technical papers/presentations

Langholtz, M., 2021, "RNG+NG+CCS: Assessment of the Potential for Decarbonization of NG with RNG and Bioenergy with Carbon Capture and Storage." Project Kickoff Meeting. DOE/NETL. Pittsburgh, PA. *https://netl.doe.gov/projects/plp-download.aspx?id=11789&filename=Assessment+of+the+Potential+for+Decarbonization+of+NG+with+RNG+and+Bioenergy+with+Carbon+Capture+and+Storage.pptx*.

Bioenergy Knowledge Discovery Framework (KDF), 2016, "Billion-Ton Report - Advancing Domestic Resources for a Thriving Bioeconomy." U.S. Department of Energy, Oak Ridge National Laboratory. Oak Ridge, TN. *https://bioenergykdf.net/2016-billion-ton-report*.

King City Asbestos Corporation Mine Carbon Mineralization Field Test

primary project goal

Lawrence Livermore National Laboratory (LLNL) is evaluating various approaches to carbon dioxide (CO_2) mineralization of asbestos-bearing serpentinite rocks/mine tailings to determine the most successful approach and to enable the U.S. Department of Energy (DOE) and project developers to make informed choices about this pathway of carbon removal.

technical goals

- Develop safety protocols to protect human health and the environment.
- Develop monitoring protocols to reliably and cost-effectively measure CO_2 uptake.
- Demonstrate enhanced weathering methodologies that increase the uptake of CO_2 by two to five times compared to the background rate.
- Achieve greater than 90% carbonation of brucite and labile magnesium (Mg).
- Show that the proportion of atmospheric carbon incorporated into newly formed carbonate minerals is significantly higher than the proportion of incorporated recycled bedrock carbon and/or biogenic carbon.
- Establish that the full life cycle CO_2 budget is net-negative.
- Develop and accelerate processes that result in CO_2 removal costs of less than \$100/tonne CO_2.
- Demonstrate site restoration to the original condition or better.

technical content

Enhanced weathering is a technique that accelerates the natural process of chemical weathering in order to absorb atmospheric CO_2 more quickly than would occur naturally. The natural process of chemical weathering is shown in Figure 1, where broken-down silicate minerals chemically react with CO_2 to form new carbonate minerals that lock CO_2 away. However, this natural process captures CO_2 at about the same rate that it is released into the atmosphere by volcanic activity. The process of accelerated carbon mineralization through enhanced weathering aims to capture CO_2 more quickly than is possible through natural chemical weathering, whereby the carbon balance is shifted to net-negative. The process of accelerated carbon mineralization has three primary rate-limiting factors: the CO_2 supply, mineral dissolution, and carbonate precipitation. However, techniques, such as those in the ovals of Figure 2, can be used to speed up the natural carbonation process and thus result in enhanced weathering and accelerated CO_2 capture and storage (CCS).

The concept of accelerating carbon mineralization has been recognized as a promising approach to remove CO_2 from the atmosphere; however, the concept has largely been explored on the bench scale or in small field trails. Assessing the potential viability of this technology and advancing the field requires larger-scale field trials, as is the focus of this work.

program area:
Carbon Dioxide Removal

ending scale:
Small Pilot

application:
Enhanced Mineralization

key technology:
Novel Concepts

project focus:
Field Testing of Accelerated Carbon Mineralization Approaches

participant:
Lawrence Livermore National Laboratory

project number:
FWP-FEW0278

predecessor projects:
N/A

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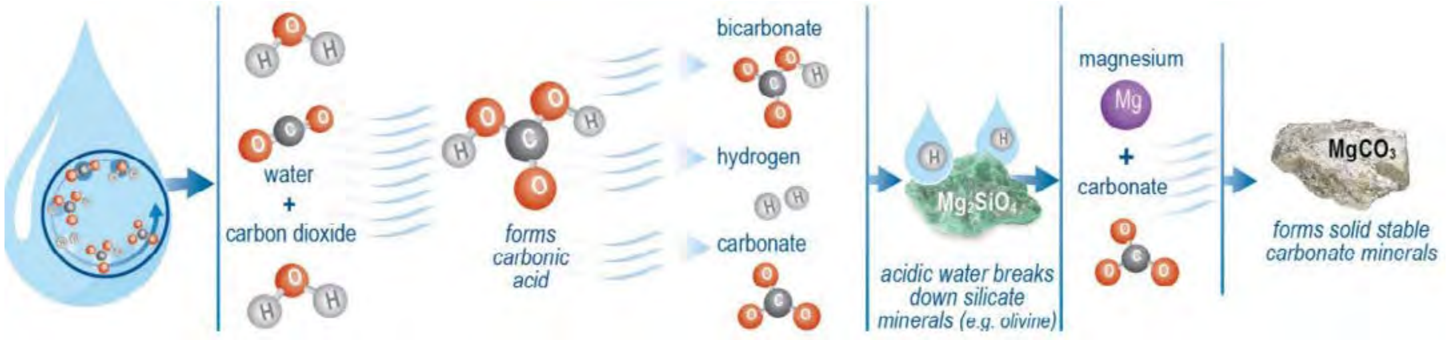
partners:
Natural Resources Agency of California; Bureau of Land Management; University of British Columbia

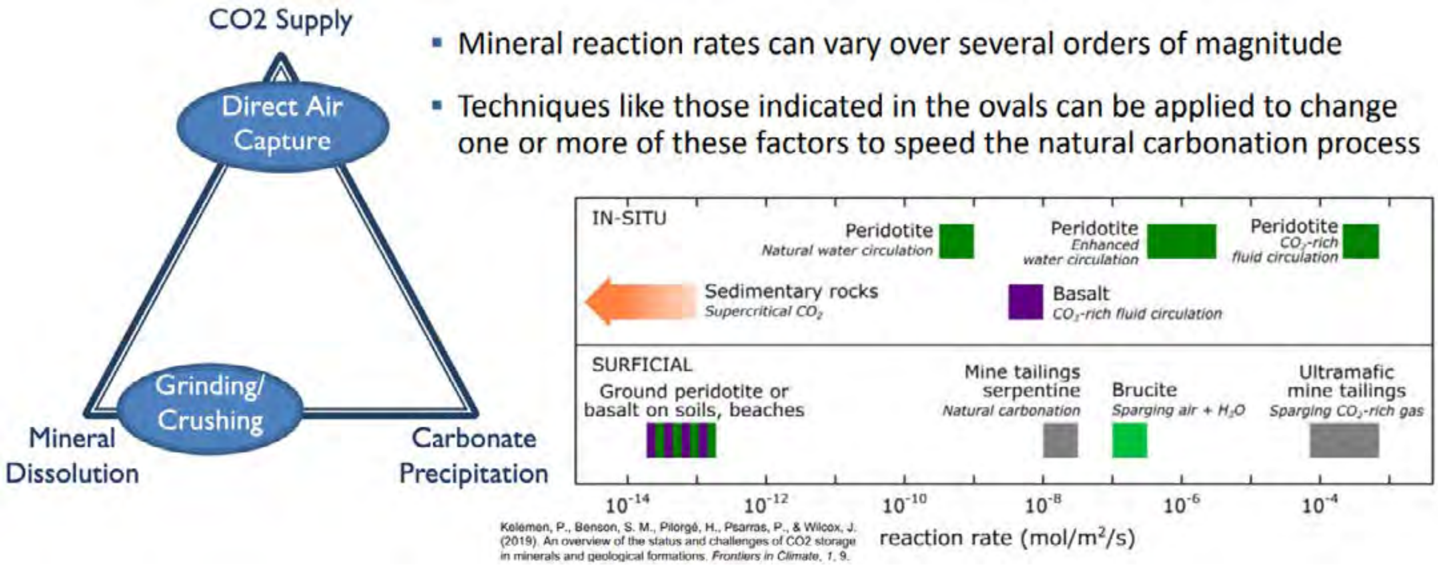
start date:
09.01.2021

percent complete:
25%



Chemical weathering draws down ~0.3 Gt CO_2/y, which over geologic timescales is approximately balanced by the amount of CO_2 released from volcanoes.

Figure 1: Natural chemical weathering and CO_2 capture.



Kelemen, P., Benson, S. M., Pilorgé, H., Psarras, P., & Wilcox, J. (2019). An overview of the status and challenges of CO2 storage in minerals and geological formations. *Frontiers in Climate*, 1, 9.

Figure 2: CO_2 mineralization influences and rates.

The former asbestos mine, King City Asbestos Corporation (KCAC) Joe Pit Mine, in San Benito County, California, has been chosen as the host site for this work as it is an ideal site for evaluating and conducting field trials for enhanced CO_2 mineralization due to the presence of serpentinite rocks and mine tailings. As shown in Figure 3, this site is located in the New Idria Serpentinite Body. Published literature indicates that the area has a brucite content of 7–8 wt% on average and 10–25 wt% in serpentinite boulders, while the magnesium oxide (MgO) content is about 40 wt%. The presence of these serpentinite minerals is highly favorable, as the potential for CO_2 mineralization is high; Figure 4 highlights the tons of CO_2 that can be stored per ton of dissolving and precipitating mineral.

California's ultramafic rocks, mostly serpentinite, cover surprising amounts of the state's land. Arrow points to the New Idria Serpentinite Body.

Figure 3: Location of California's ultramafic rocks (mostly serpentinite).

Tons of CO_2 sequestered per ton of dissolving and precipitating mineral

Dissolving Mineral	Precipitating Mineral	Name	Magnesite	Hydromagnesite	Dypingite	Pokrovskite	Artinite	Nesquehonite	Lansfordite
		Formula	$MgCO_3$	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	$Mg_5(CO_3)_4(OH)_2 \cdot {\sim}5H_2O$	$Mg_2(CO_3)(OH)_2$	$Mg_2(CO_3)(OH)_2 \cdot 3H_2O$	$MgCO_3 \cdot 3H_2O$	$MgCO_3 \cdot 5H_2O$
Name	Formula	CO_2: MgO ratio	1:1	4:5	4:5	1:2	1:2	1:1	1:1
Serpentine[a]	$[Mg_3Si_2O_5(OH)_4]$	-	0.48	0.38	0.38	0.24	0.24	0.48	0.48
Brucite	$[Mg(OH)_2]$	-	0.75	0.60	0.60	0.38	0.38	0.75	0.75
Forsterite	$[Mg_2SiO_4]$	-	0.63	0.50	0.50	0.31	0.31	0.63	0.63
Diopside[b]	$[CaMgSi_2O_6]$	-	0.41	0.37	0.37	0.30	0.30	0.41	0.41
Enstatite	$[Mg_2Si_2O_6]$	-	0.44	0.35	0.35	0.22	0.22	0.44	0.44

Modified from I. M. Power, A. L. Harrison, G. M. Dipple, S. A. Wilson, P. B. Kelemen, M. Hitch, G. Southam, Carbon Mineralization: From Natural Analogues to Engineered Systems. Reviews in Mineralogy and Geochemistry. 77, 305–360 (2013).

Figure 4: Amount of CO_2 stored per ton of dissolving and precipitating mineral.

Project Concept and Overview

LLNL is establishing the test design, test characterization, and baseline measurement methodologies at the test site located at the KCAC Joe Pit Mine, shown in Figure 5. Various approaches for onsite mineralization of CO_2 using serpentinite rocks and asbestos tailings are being tested and compared to gain information to enable DOE to make informed decisions regarding enhanced weathering processes, as well as regarding the human health and environmental safety factors. Furthermore, restoring the site to its original condition (or better) will be implimented and evaluated.

Figure 5: Location of test site at the KCAC Joe Pit Mine.

This work entails the development of an environmental, health, and safety (EH&S) plan for working at the KCAC test site. The handling of asbestos-containing material requires training and monitoring for all site users and the implementation methodologies established in this work will be informative to potential future developments. This work also involves establishing how baseline conditions and natural variability should be taken into consideration. For instance, the CO_2 flux, water cycling at the site, and aqueous chemical characteristics must all be understood in terms of baseline values considering seasonal variations. This information then informs the design of the carbon mineralization field experiements, which could be conducted using passive or more involved experimental methods, such as more frequently stirring reactive material to increase air contact or constructing purpose-built facilities to control the ambient conditions. It is anticipated that field experiments will be conducted on the scale of tons to tens of tons of reactive material. LLNL aims to advance the technology readiness from its current TRL 2 to TRL 5 during the course of this project.

technology advantages

- Accelerates the natural mineralization process to capture CO_2.
- Potential for a net-negative CO_2 budget.
- Potential for large-scale CO_2 storage.

R&D challenges

- Human health hazards due to exposure to asbestos-bearing serpentinite rocks/mine tailings.
- Environmental hazards due to disturbance of asbestos-bearing serpentinite rocks/mine tailings.
- Effective monitoring of CO_2 flux and uptake.
- Developing successful accelerated carbon mineralization experiments at low cost.

status

The project team is conducting initial site characterizations, is currently developing the EH&S plan, and is making progress toward determining a final evaluation design based on baseline measurements.

available reports/technical papers/presentations

“King City Asbestos Corporation (KCAC) Mine Carbon Mineralization Field Test,” Project Kickoff Meeting, March 14, 2022. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13020&filename=King+City+Asbestos+Corporation+(KCAC)+Mine+Carbon+Mineralization+Field+Test.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

RESEARCH AND DEVELOPMENT COLLABORATIONS

National Carbon Capture Center

primary project goal

The U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) and Southern Company operate the National Carbon Capture Center (NCCC), a neutral research facility working to advance technologies to reduce greenhouse gas emissions from fossil-based power plants and industrial processes and to promote carbon utilization and direct air capture (DAC) innovations. Located in Wilsonville, Alabama, the center offers a unique test bed for third-party evaluations of cost-effective carbon dioxide (CO_2) capture technologies—bridging the gap between laboratory research and large-scale demonstrations.

The NCCC offers exceptional benefits to technology developers by providing them with testing opportunities in the real-world operating conditions of a power plant, thereby accelerating the commercialization of low-cost, carbon capture processes. The center has surpassed 125,000 hours of testing for carbon capture innovators from the United States and six other countries. Through the testing of 70 technologies, the center has directly participated in the reduction of the projected cost of CO_2 capture by approximately 40%.

The NCCC, shown at left, supports the evaluation of advanced technologies from both domestic and international developers. These evaluations are critical in identifying and resolving environmental, health and safety, operational, component, and system development issues, as well as achieving scale-ups and process enhancements in collaboration with technology developers. DOE-sponsored projects, as well as projects from industry, universities, and other collaborative institutions, provide a full spectrum of technologies for testing at the center.

technical content

The DOE Office of Fossil Energy and Carbon Management's (FECM) NETL, in cooperation with Southern Company, established the NCCC in 2009 to provide an independent, flexible, cost-efficient carbon capture testing facility with industrial operating conditions. Since its inception, researchers at the NCCC have conducted numerous tests for the advancement of post-combustion carbon capture for coal and natural gas power plants. Early testing also included more than 30 projects in the gasification and pre-combustion carbon capture areas, a scope of work that has since concluded. In 2020, the NCCC added new infrastructure to broaden its post-combustion test capabilities under actual natural gas-fired conditions. Additionally, the center has begun to host CO_2 utilization and

project focus:

Carbon Capture Testing Center

participant:

Southern Company

project number:

FE0022596

predecessor projects:

NT0000749

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partners:

American Electric Power; BP; ClearPath Foundation; Electric Power Research Institute; ExxonMobil; NRECA; Peabody; Tennessee Valley Authority; TotalEnergies; Wyoming Integrated Test Center

start date:

06.06.2014

percent complete:

70%

DAC technologies, as well as carbon capture process intensification projects. The testing infrastructure supports the capability to test hybrid concepts that include both DAC and CO_2 capture from concentrated sources.

The NCCC's post-combustion test facilities operate at Alabama Power's Plant Gaston with flue gas supplied from the center's natural gas boiler and Plant Gaston Unit 5, a commercial, base-loaded, 880-megawatt (MW) supercritical pulverized coal-fueled unit. The natural gas boiler produces flue gas representative of that from a commercial natural gas combined-cycle power plant. The NCCC provides test bays for simultaneous lab-, bench- and pilot-scale operation of advanced carbon capture technologies at commercially relevant process conditions. These include two fully integrated processes for solvent evaluations—a pilot-scale test unit (PSTU) and a bench-scale slipstream solvent test unit (SSTU)—as well as seven pilot- and bench-scale test bays and an indoor lab-scale test area. The center also provides support for design, procurement, construction, installation, operation, data collection and analysis, and reporting in compliance with environmental and government requirements. Figure 1 shows the test facilities and the natural gas and coal flue gas configurations.

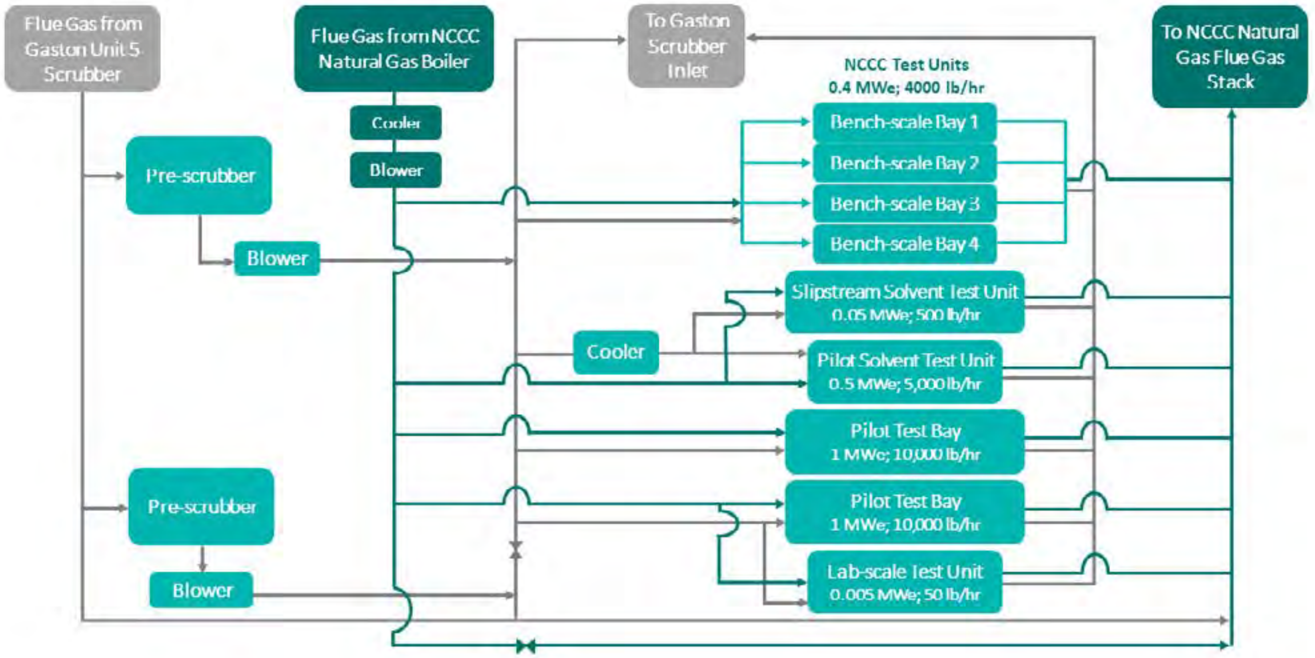

Figure 1: Diagram of post-combustion test facilities at the National Carbon Capture Center.

The PSTU is a nominal 0.5-megawatt-electric (MWe) solvent-based CO_2 capture absorber/stripper system designed to process a flow rate of 5,000 pounds per hour (lb/hr) coal-derived flue gas or up to 8,000 lb/hr natural gas-derived flue gas. The major components of the system are a pre-scrubber, cooler/condenser, absorber, wash tower, and regenerator. The PSTU has three options available for solvent regeneration to release the CO_2 from the solvent:

1. A packed-bed column regenerator that provides heat via steam in a sump-located pump-around loop with a shell and tube heat exchanger to release CO_2 in a conventional simple stripper configuration.
2. A continuous stirred tank reactor (CSTR), designed by GE Global Research for their testing, which is a one-stage separation unit with reduced space requirements and potentially lower capital requirements compared to conventional regenerator columns.
3. An advanced flash stripper, developed by the University of Texas at Austin and AECOM for their testing, which recovers the stripping steam heat by employing cold and warm rich bypasses.

The SSTU is a 0.05-MWe solvent-based CO_2 absorber/regenerator system with the ability to test innovative CO_2 capture solvents under a variety of conditions using up to 500 lb/hr of flue gas. The SSTU is optimized for validating lab-based results under industrial conditions to yield scalable data for further pilot-scale testing.

technology advantages

The NCCC's ability to support multiple developers and tests simultaneously at various scales, and to offer flexibility in capacity and process conditions, offers a wide range of data and information to accelerate the commercialization of CO_2 capture and utilization technologies. The NCCC also offers advantages to DAC developers, including a proficient staff, the capability to test both DAC and capture from concentrated sources (or hybrid concepts), and assistance in finding domestic and international partners for scale-up.

R&D challenges

The NCCC's state-of-the-art facility, which delivers necessary infrastructure, flue gases, utilities, and other support, enables the effects of system interactions to be understood to ensure a smooth transition of technologies from a laboratory setting to an industrial setting. By executing field-testing under realistic power plant conditions, technologies can be scaled-up with confidence for larger-scale demonstrations. For technologies that are not ready for scale-up, improvements are identified, and further engineering-scale testing needs are defined.

status

NCCC operation has provided more than 75,000 hours of testing enzymes, membranes, sorbents, solvents, hybrids, and associated systems for post-combustion carbon capture, as well as CO_2 utilization technologies, and included 46 technologies from 33 developers, with eight technologies scaled-up (or ready) to be demonstrated at 10+ MW. More than 8,000 hours of testing has been conducted under simulated natural gas conditions. In addition, test campaigns are planned for DAC technologies. The PSTU has operated for more than 24,000 hours in support of commercial developers and DOE's Carbon Capture Simulation Initiative, with several technologies progressing to larger-scale testing at other facilities and commercial demonstration. Since its creation, the NCCC has more than tripled its plant capacity from 12,000 to 40,000 lb/hr flue gas and has added systems (lab-scale test unit [LSTU], advanced flash stripper, natural gas flue gas infrastructure, etc.), along with enhanced instrumentation, sampling methods, and analysis systems. Performance data generated in technology testing at the NCCC has been used to validate laboratory data allowing for engineering scale-up and, in turn, driving new breakthroughs in carbon capture solutions.

available reports/technical papers/presentations

"National Carbon Capture Center Technology Testing Update (FE002256)," presented by Tony Wu, Southern Company, 2021 NETL Carbon Management and Oil and Gas Research Project Review Meeting, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Wu.pdf*.

"Carbon Utilization and the National Carbon Capture Center," presented by John Northington, Southern Company, 2020 NETL Integrated Project Review Meeting – Carbon Utilization, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCU_Northington.pdf*.

"Advanced Carbon Capture Testing at the National Carbon Capture Center (FE0022596)", presented by Michele Corser, Southern Company, 2019 NETL Carbon Capture, Utilization and Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Corser-Southern-Co-NCCC-Testing.pdf*.

"Status of Technology Development at the National Carbon Capture Center," presented by Justin Anthony, John Carroll, Michele Corser, Frank Morton, Tony Wu, and Ruth Ann Yongue, Southern Company, International Conference on Greenhouse Gas Control Technologies, GHGT-14, October 2018. *https://papers.ssrn.com/sol3/papers.cfm?abstract_id=3366390.*

"Update on National Carbon Capture Center (FE0022596)," presented by Tony Wu, Southern Company, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/netl-file/T-Wu-Southern-National-Carbon-Capture-Center.pdf*.

"Advanced Technology Testing at the National Carbon Capture Center (FE0022596)," presented by John Carroll, Southern Company, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File Library/Events/2017/co2 capture/1-Monday/J-Carroll-Southern-National-Carbon-Capture-Center.pdf*.

"Advanced Technology Testing at the National Carbon Capture Center," presented by Justin Anthony and John Carroll, Southern Company, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File Library/Events/2016/c02 cap review/1-Monday/J-Anthony-SouthernCo-Testing-at-National-Carbon-Capture-Center.pdf*.

National Carbon Capture Center website: *https://www.nationalcarboncapturecenter.com/*.

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